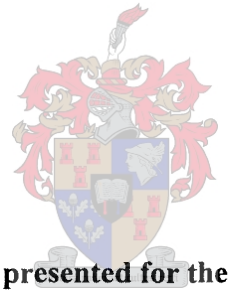
STRUCTURE/PROPERTY RELATIONSHIP OF MODEL ALKALI-SOLUBLE RHEOLOGY MODIFIERS SYNTHESISED VIA THE RAFT PROCESS

by

EWAN SPRONG



Dissertation presented for the degree of

Doctor of Philosophy (Polymer Science)

at the

University of Stellenbosch

Promoter: Prof. R. D. Sanderson

Stellenbosch

December 2003

DECLARATION

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Ewan Sprong

ABSTRACT

Alkali-soluble rheology modifiers are commercially synthesised via conventional free-radical polymerisation processes. This results in the end product having certain limitations; there is poor control over the molar mass, molar mass distribution and chain architecture of the polymer chains. These limitations can be overcome by using a controlled/living free radical polymerisation process, for example the RAFT process. This alternate method of synthesis was used here to prepare model alkali-soluble rheology modifiers. The structure/property relationships of model alkali-soluble rheology modifiers synthesised via the RAFT process were studied.

Model alkali-soluble rheology modifiers of different molar masses and chain architectures (block, co- and ter-polymers) were successfully synthesised by the RAFT polymerisation of methyl methacrylate, methacrylic acid and various hydrophobic macromonomers.

The different types of alkali-soluble rheology modifiers were synthesised in solution and in miniemulsion. Each of the two systems had certain advantages and disadvantages. The conversion limit of reactions in solution was about 60 % and reaction times were much slower than those of the miniemulsion reactions. Higher final conversions were recorded for miniemulsion reactions, reactions were faster and no solvent removal was required. Unfortunately it was not possible to synthesise all the different types of associative rheology modifiers investigated here in a miniemulsion system.

The latex solutions thickened with conventional rheology modifiers (co-polymers) show very contrasting behaviour (rheology profile and dynamic properties) to that of the latex solutions thickened with the associative rheology modifiers (ter-polymers). The AB block copolymers gave the latex solutions rheology results between those obtained with conventional rheology modifiers and those with the associative rheology modifiers. Varying the number of ethylene oxide spacer units in the hydrophobic macromonomers of the associative rheology modifiers had a significant influence on the rheology properties of the latex and alkali solutions. As the number of ethylene oxide spacer units

was increased from 20 to 100 there was a significant increase in the zero-shear viscosity of the latex solutions thickened with the associative rheology modifiers. Contrasting results were obtained for the polymer solutions (no latex present), where the use of the associative rheology modifiers containing the highest number (EO = 100) of ethylene oxide spacer units resulted in solutions with the lowest viscosity, but the rheology modifiers containing the 50 ethylene oxide spacer units gave the highest steady shear viscosity.

OPSOMMING

Alkali-oplosbare reologie-modifiseerders word kommersieël gesintetiseer d.m.v. konvensionele vrye-radikaal polimerisasieprosesse. Hierdie prosesse lewer gewoonlik 'n eindproduk met sekere tekortkominge, a.g.v. swak beheer oor molekulêre massa, molekulêre massa-verspreiding, en polimeerkettingstruktuur (Eng. chain architecture). Hierdie tekortkominge kan oorbrug word deur gebruik te maak van 'n beheerde/lewende vrye-radikaal polimerisasieproses, soos byvoorbeeld die RAFT-proses (Eng. RAFT: reversible addition-fragmentation chain transfer polymerisation). Hierdie alternatiewe metode is in die studie gebruik om model alkali-oplosbare reologiemodifiseerders te sintetiseer. Die struktuur-eienskapverhoudings van die model alkali-oplosbare reologie modifiseerders wat d.m.v. die RAFT-proses gesintetiseer is, is bestudeer.

Model alkali-oplosbare reologiemodifiseerders van verskillende molekulêre massas en kettingstrukture (blok, ko- en ter-polimere) is suksesvol gesintetiseer d.m.v. RAFT-polimerisasie van metielakrilaat, metakrielsuur en hidrofobiese makromonomere.

Die verskillende alkali-oplosbare reologiemodifiseerders is in organiese oplosmiddel sowel as in mini-emulsie gesintetiseer. Elkeen van die sisteme het sekere voordele en nadele getoon. In die reaksies wat in organiese oplosmiddels gedoen is, is slegs 60 % van die monomere ingebou in die polimeerkettings en die tydsduur van hierdie reaksie was heelwat langer as by die wat uitgevoer is in mini-emulsie. Meer as 60 % van die monomere is omgeskakel na polimeer tydens die reaksies wat in mini-emulsie uitgevoer is, die reaksietempo was vinniger en dit was nie nodig om die organiese oplosmiddel te verwyder nie. Ongelukkig was dit nie moontlik om al die verskillende tipes assosiatiewe-reologiemodifiseerders (Eng: associative rheology modifiers) in mini-emulsie te sintetiseer nie.

Die lateks wat met konvensionele reologiemodifiseerders (ko-polimere) verdik is, het kontrasterende eienskappe (reologie-profiel en dinamiese eienskappe) getoon teenoor die van die lateks-oplossings wat met assosiatiewe-reologiemodifiseerders (ter-polimere) verdik is. Die AB-tipe blok ko-polimere gee reologieresultate vir die lateks-oplossings wat lê tussen die wat bepaal is vir konvensionele reologieodifiseerders en assosiatiewe

reologiemodifiseerders. Variasie in die aantal etileenoksiedeenhede in die hidrofobiese makromonomere van die assosiatiewe reologiemodifiseerders het 'n betekenisvolle invloed op die reologie-eienskappe van die lateks, sowel as die alkali-oplossings gehad. Namate die aantal etileenoksiedeenhede van 20 tot 100 vermeerder is, het 'n betekenisvolle verhoging in die "zero-shear " viskositeit van die lateks oplossings wat met die assosiatiewe reologiemodifiseerders verdik is voorgekom. Teenstrydige resultate is verkry vir die polimeeroplossings met geen lateks teenwoordig nie: die assosiatiewe reologiemodifiseerders met die hoogste aantal etieleenoksiedeenhede (EO = 100) het die laagste viskositeitsresultate opgelewer en die reologiemodifiseerders met slegs 50 etieleenoksiedeenhede het die hoogste viskositeitsresultate gelewer .

ACKNOWLEDGEMENTS

The author would like to convey his sincere thanks to the following:

Prof. Ron Sanderson (promotor) for his interest, enthusiasm and assistance in my chosen field of research.

Dr. Deon de Wet-Roos for all his help, ideas and endless patience with the research project.

Dr. Matthew Tonge for all the fruitful discussions and help in interpreting the experimental results.

The Department of Chemistry and Polymer Science, University of Stellenbosch and the National Research Foundation for financial support.

The staff at Polymer Science, especially Aneli, Margie, Erinda and Calvin.

Jean McKenzie and Elsa Malherbe for the running of NMR samples.

Sastech R&D, Sasol Technology (Pty) Limited for the use of their Paar Physica MCR 300 rheometer.

Plascon Research Centre for the use of their Paar Physica MCR 300 rheometer.

On a more personnel note I would like to thank my parents for their support, encouragement and the opportunity they gave me to further my studies.

Tanya, thanks for all your love and support through the many long nights I spent working on the thesis.

To all my friends at Polymer Science, especially the Free Radical Group (Andre, Malan, Matthew, James, Jaco, Andrew and Ingrid), thanks for all the ideas and laughs we could share.

Thanks to Hein, Cornelia, Andre, Susan, Tokkie and Piet (friends outside of Polymer Science) for all the good times we could share together and all your support during my studies.

Thank you very much everybody!

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NOTATION

$\bar{M}_n$	number average molar mass
$\bar{M}_w$	weight average molar mass
$\bar{M}_{n,\,theory}$	calculated number average molar mass
$[I]_0$	initial concentration of the initiator
$[M]_0$	initial concentration of the monomer
$[RAFT]_0$	initial concentration of the RAFT agent
AA	acrylic acid
AIBN	2,2-azobis(isobutyronitrile)
AST	alkali-swellable or alkali-soluble thickener
ATRP	atom transfer radical polymerisation
BA	butyl acrylate
DMSO	dimethyl sulfoxide
FTIR	fourier transform infrared spectroscopy
FW_M	molar mass of a monomer unit
FW_{RAFT}	molar mass of RAFT agent
HASE	hydrophobically modified alkali soluble (or swellable) emulsion
HD	hexadecane
HEC	hydroxyethyl cellulose
HEUR	hydrophobically modified ethylene oxide urethane
HM 1	hydrophobic macromonomer one (5 ethylene oxide spacer units)

HM 2	hydrophobic macromonomer two (20 ethylene oxide spacer units)
HM 3	hydrophobic macromonomer three (50 ethylene oxide spacer units)
HM 4	hydrophobic macromonomer four (100 ethylene oxide spacer units)
HMHEC	hydrophobically modified hydroxyethyl cellulose
HPAM	hydrophobically modified polyacrylamide
HWSP	hydrophobically modified water-swellable or water-soluble polymers
KPS	potassium persulfate
MAA	methacrylic acid
MMA	methyl methacrylate
PMMA	poly(methyl methacrylate)
Polystep B-27	nonylphenoxypolyethyleneoxyethanol sulfate
RAFT	reversible addition-fragmentation chain transfer
SEC	size exclusion chromatography
THF	tetrahydrofuran
WSP	water-swellable or water-soluble polymers
$\dot{\gamma}$	shear rate
ω	angular velocity
γ	deformation
σ	surface tension of the liquid-liquid interface
η	viscosity
ν_b	volume of a single molecule
$\Delta\mu$	difference in chemical potential
f_I	initiator efficiency
G	shear modulus

G'	storage modulus
G"	loss modulus
K	fluid "consistency index"
k_β	rate coefficient
k_B	Boltzmann's constant
k_d	decomposition rate coefficient for the initiator
k_p	propagation rate coefficient
N	Carreau exponent
n	power law index
r	radius of the droplet
τ	shear stress
T	absolute temperature
u_p	plastic viscosity
x	fractional conversion.
μ_b	chemical potential of bulk material
μ_d	chemical potential of droplet material
η_∞	infinite shear viscosity
η_0	zero shear viscosity
λ	Carreau constant
τ_0	yield stress

CHAPTER 1

Introduction and Objectives

1.1 Introduction

A wide variety of rheology modifiers are used today to adjust or modify the rheology properties (profile) of a number of products synthesised commercially. The coatings industry is an example of a product area that relies on the use of rheology modifiers to provide their products with the necessary flow properties to satisfy customer demands. Application properties of latex paints rely on the use of rheological additives and modifiers to a much greater extent than their solvent-based counter parts. Depending on the properties desired for a given end use market, a typical latex paint may contain up to four rheological additives. Typically a combination of additives is used to produce a good balance of container viscosity, application viscosity, anti-settling properties, spatter resistance, flow, and levelling. Figure 1.1 shows a generalised presentation of a rheology profile and the application properties.

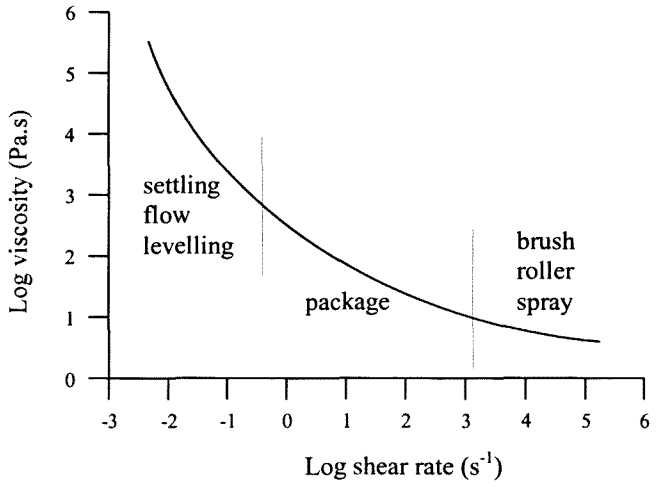


Figure 1.1: Generalised presentation of a rheology profile and the application properties. Each of the different shear rate zones corresponds to a specific application property.

Hydroxyethyl cellulose thickeners (HEC),[1-3] hydrophobically modified ethylene oxide urethane rheology modifiers (HEUR),[4, 5] and alkali-soluble thickeners/rheology modifiers (AST)[6, 7] are the most common types of thickeners/rheology modifiers used in the paint industry.

HEC is not an associative thickener and provides rheology by thickening the water phase of the paint. HEC has little interaction with other paint ingredients. At rest, the viscosity of a paint system containing a cellulose thickener (low shear rate viscosity) is very high and in some cases the paint at rest approaches a gelled state. As higher shear is applied to the paint, either by simple stirring or by brush or roller, the viscosity drops considerably, allowing easy application and a creamy smooth appearance. After the high shear is removed, the paint rapidly returns to its original high viscosity. Cellulose thickeners, although virtually non-reactive in the paint, are often deficient in providing some basic applications requirements. Because of the fast recovery rate of the paint system, and the short time scale of the gel phase at low shear rates, paint containing cellulose thickeners have poor levelling and flow, and poor spatter resistance. The hydrophobically modified cellulose thickeners increase the paints mechanical properties, improve spatter resistance, and flow properties. The hydrophobic modification also makes the cellulose molecule more interactive with other paint ingredients, and consequently, more associative in the system. The associative behaviour of hydrophobically modified cellulose can interfere with colour acceptance properties and stability in the paint can.

The study of the structure/property relationship of HEUR rheology modifiers has received much more attention in literature than have cellulose thickeners and alkali-soluble rheology modifiers. The reason for this is the relative ease with which tailored model compound HEUR rheology modifiers can be made, where the structure of the polymer is known and it can therefore be related to the rheology properties subsequently obtained. Model HEUR rheology modifiers can be synthesised by the stepwise addition of tri or di or mono isocyanates to poly(ethylene oxide)diols, followed by the reaction of the terminal isocyanate groups with hydrophobic alcohols and or amines. By varying the type of isocyanate and length of the poly(ethylene oxide)diols, it is easy to synthesise a number of structurally different HEUR rheology modifiers.[4,5] The main structure/property relationship studies carried out on HEUR rheology modifiers involve

changing the type of hydrophobic component (isocyanate group and hydrophobic alcohols), the amount of hydrophobes in the polymer chains, and the length of the hydrophilic segment(s) (polyethylene oxide) connecting the hydrophobic segments to each other. It has been shown the high shear viscosity increases with increasing segment length of the hydrophobe from C_{13} to C_{18}.[8] Increasing the mole ratio of the ethylene oxide/hydrophobic segment increases the viscosity until the concentration of the hydrophobes falls below an effective level.[4] HEUR rheology modifiers are non-ionic in nature and do not need pH adjustment. Their thickening behaviour is achieved through association with the pigments, binders and surfactants in the system.

Alkali-soluble rheology modifiers are synthesised by means of conventional free radical polymerisation of a number of different types of ethylenically unsaturated monomers and hydrophobic macromonomers.[9,10] Commercially, the associative alkali-soluble rheology modifiers are synthesised in emulsion and are referred to as hydrophobically modified alkali-soluble emulsions (HASE). It is relatively easy to synthesise rheology modifiers with different structures by merely changing the types of monomers used. However, the syntheses of the aforementioned polymers follow conventional free radical polymerisation routes and therefore have related process limitations, such as poor control over the molar mass, molar mass distribution, end group functionalities, and chain architecture of the polymers.

The fairly recent development of living polymerisation techniques such as nitroxide-mediated controlled radical polymerisation (NMCRP),[11,12] atom transfer radical polymerisation (ATRP)[13,14] and reversible addition-fragmentation chain transfer (RAFT) polymerisation[15,16] have brought new advantages to the free radical polymerisation synthesis of polymers. These techniques allow the synthesis of polymers of controlled molar mass, narrow polydispersity and tailored chain architecture. The ability to control the architecture and molar mass properties of alkali-soluble rheology modifiers will give one the tool to design rheology modifiers that will give the specific rheological properties desired for a specific coating system. Some structure/property relationship studies have been carried out for HASE thickeners, such as the effect of varying the hydrophobe chain length.[10] Although it is possible to control the hydrophobe chain length, the polymer

backbone is still synthesised by means of conventional uncontrolled radical polymerisation.

Controlled polymerisation of these model alkali-soluble rheology modifiers in miniemulsion will have the advantage of producing products that are easy to handle (low viscosity latex), absence of organic solvents and high conversions can be reached in a short time. Controlled radical polymerisation allows the synthesis of compounds that allow the study of the structure/property relationship of alkali-soluble rheology modifiers, which are important objectives for this study; these objectives are stated in the next section.

1.2 Objectives and outline

The first objective of this research endeavour was to synthesis different model alkali-soluble rheology modifiers with good control over the molar mass, molar mass distribution and chain architecture. Secondly, once these model compounds were synthesised, their rheological properties were analysed (in alkali-solution and in a latex solution) and their structure/property relationships investigated. The rheology modifiers were synthesised by means of RAFT polymerisation in solution and in miniemulsion. The reason for this was to obtain a better and more detailed understanding of the structure/property relationship of alkali-soluble rheology modifiers.

The following section describes the contents of the thesis as well as the objectives of the individual chapters:

Chapter 2 gives some relevant background and theoretical aspects of rheology, thickeners/rheology modifiers and controlled/living polymerisation. The first section describes different flow behaviours observed in viscous substances and attempts to explain the concept of viscoelasticity of polymers by means of some simple theoretical models. The second section describes some of the various types of thickeners/rheology modifiers used in industry. Their structural differences, thickening mechanisms and rheological properties are discussed and compared. In the final section the

controlled/living polymerisation techniques NMCRP and ATRP are discussed briefly, with a more detailed look at the kinetic and mechanistic aspects of the RAFT process. The RAFT process was chosen as the living polymerisation technique in this study because of its versatility with respect to choice of monomer and reaction conditions. Other choices of controlled radical polymerisation techniques are more limited in these respects. Nitroxide mediated polymerisation is useful for a limited range of monomers, and reaction temperatures are usually high. ATRP is a more versatile technique, but is limited with respect to monomer choice. For the monomers used in the current study, the use of the metal ions in ATRP might lead to complications due to interactions with the acid functionality of the methacrylic acid component. Moreover, the removal of these metal ions from the final polymer is problematic. In the case of the RAFT process, the dithioesters used to mediate the process can easily be removed from the polymer chains by the addition of a base (e.g. NaOH) without changing the mechanical properties of the polymer chains.

In Chapter 3, the syntheses of different alkali-soluble rheology modifiers by the *in situ* RAFT solution reaction of AIBN, bis(thiocarbonyl) disulfide (a coupled RAFT agent), methyl methacrylate, methacrylic acid and hydrophobic macromonomers are described. The rheological properties of the synthesised rheology modifiers are tested in a well-characterised core-shell emulsion and related to the structural differences between the different rheology modifiers. The main structural differences studied were that of conventional (no hydrophobic macromonomer) vs. associative rheology modifiers (hydrophobic macromonomers incorporated randomly). The third type of structure investigated (also an associative rheology modifier) was the addition of the hydrophobic macromonomer as a second block onto one end of the polymer chains of a conventional rheology modifier (i.e. formation of an AB block copolymer).

Chapter 4 investigates rheological properties of conventional and associative alkali-soluble rheology modifiers synthesised in solution using 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid as the RAFT agent. Different types of associative

alkali-soluble rheology modifiers are synthesised by using hydrophobic macromonomers containing different ethylene oxide spacer units. The three hydrophobic macromonomers used contained 20 (HM2), 50 (HM3) and 100 (HM4) ethylene oxide spacer units, respectively. For each of the hydrophobic macromonomers, three different molar mass polymers were synthesised containing 1 % of the specific hydrophobic macromonomer. The effects of varying the molar mass and the ethylene oxide spacer units on the rheological properties of the synthesised rheology modifiers were tested in alkali-solution and in a well-characterised core-shell emulsion. The steady shear viscosity data for the emulsion solutions thickened with conventional and associative rheology modifiers are well described by the Herschel-Bulkley and Carreau models, respectively.

In Chapter 5, the syntheses of the model alkali-soluble rheology modifiers in miniemulsions, using 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid as the RAFT agent, are described. The influences of both the type of initiator (oil-soluble or water-soluble) as well as the percentage of MAA used in the miniemulsion system on the polymerisation reactions are investigated. The amount of associative macromonomer (HM1) incorporated into the polymer chains of the associative rheology modifiers, was varied from 1% – 5 % and the influences they have on the rheological properties of the rheology modifiers are studied.

Chapter 6 gives a summary of the overall conclusions reached in the studies on the structure/property relationship of the different model alkali-soluble rheology modifiers synthesised via the RAFT process and some suggestions for further work that could be carried out.

1.3 References

1 Just, E. K.; Majewicz, T. G. *Encyclopedia of Polymer Science and Engineering*, Wiley-Interscience, New York, 1985, 17, 226.

2 Croll, S. G.; Kleinlein, R. L. *Water Soluble Polymers: Beauty with Performance*, American Chemical Society, Washington, D.C., 1986, 333.

3 Blake, D. M. *Handbook of Coatings Additives*, Marcel Dekker, New York, 1987, 1, 43.

4 Fonnum, G.; Bakke, J.; Hansen, F. K. *Colloid. Polym. Sci* 1993, 271, 380.

5 Annable, T.; Buscall, R.; Ettelai, R.; Whittlestone, D. *J. Rheol.* 1993, 37, 695.

6 LeSota, S.; Lewndowski, E. W.; Schaller, E. J. *J. Coat. Technol.* 1989, 61, 135.

7 English, R. J.; Gulati, H. S.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* 1997, 41, 427.

8 Knoef, A. J.; Slingerland, H. *Journal of Oil Colour Chemist Association* 1992, 9, 335.

9 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 1426.

10 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 3271.

11 Okamura, H.; Takatori, Y.; Tsunooka, M.; Shirai, M. *Polymer* 2002, 43, 3155.

12 Chong, B. Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. *Macromolecules* 1999, 32, 6895.

13 Wang, J.-S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.

14 Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* 2000, 33, 255.

15 Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.

16 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.

CHAPTER 2

Background

Synopsis: *This chapter gives a short overview of rheology, thickeners/rheology modifiers and controlled free radical polymerisation, which are the main focus areas of this thesis.*

In the first part of this chapter some basic aspects of viscometry and various types of flow behaviours that are observed in viscous substances are explained. The fact that polymers exhibit both elastic and viscous behaviour is described by means of several theoretical models.

Alkali-soluble polymers, especially hydrophobically modified polymers, are extensively used as thickeners and rheology modifiers in a variety of industrial products. In the second part of this chapter their characterisation and thickening mechanisms are discussed and compared to those of other well known thickeners/rheology modifiers, like cellulose thickeners and hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers.

In the last section the process of controlled free radical polymerisation is explained, with a more detailed look at reversible addition-fragmentation chain transfer (RAFT). Several characteristic kinetic and mechanistic aspects of the RAFT process are discussed.

2.1 General introduction

The aim of this chapter is to explain and describe some basic theoretical and historical aspects of rheology, thickeners/rheology modifiers and controlled free radical polymerisation.

Rheology is a complex and often difficult subject area, but a basic understanding is essential for scientists employed in many industries, such as plastics, paints, printing inks, detergents, and oils. The rheology section presents some basic aspects of viscometry and various flow behaviours that are observed for different substances. The concept of viscoelasticity is also explained by means of several simple theoretical models.

Thickeners/rheology modifiers have been used for many years to modify the viscosity and rheology of a variety of industrial products, such as paints, foods, pharmaceuticals, and personal care. The structures of cellulose thickeners, hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers and alkali-soluble rheology modifiers are discussed, along with their specific rheological properties.

Conventional free radical polymerisation is one of the most convenient and robust methods used by industry to synthesise a wide range of industrial products. The major limitation of this process is the lack of control over the polymer structure, but this can be overcome with the use of controlled free radical polymerisation techniques. Being able to control the polymer structure is an extremely important tool for structure/property studies. A number of these living free radical techniques are discussed, with a more in depth look at the reversible addition-fragmentation chain transfer (RAFT) process, which is used in the controlled synthesis of the rheology modifiers prepared and studied in this thesis.

2.2 Rheology

2.2.1 Introduction

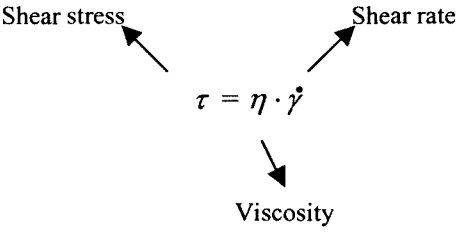
Rheology describes the deformation of a body under the influence of stresses. Bodies in this context can be solids, liquids, or gasses. Two classical ideal states describe the two extremes of rheology. At the one end lies a Hookean solid, which deforms proportionally

to the stress applied, and stores the energy to affect a complete recovery of the original state when the applied stress is removed. At the other end is a Newtonian liquid that flows proportionally to the stress applied, and shows no recovery when the stress is removed; the energy required for the deformation is dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses. Polymers exhibit neither ideal solid nor ideal liquid behaviour and their rheological behaviour is somewhere between the two ideal states. Polymers exhibit both viscous and elastic behaviour and are therefore referred to as visco-elastic materials. The Maxwell or the Kelvin-Voigt models describes this visco-elastic behaviour of polymers. These models are explained in more detail in Section 2.14. If more information is desired, the reader can refer to a general rheology textbook.[1]

2.2.2 Flow behaviour of viscous substances

2.2.2.1 The basic law

The measurement of the viscosity of liquids requires the definition of the parameters which are involved in the flow. Suitable test conditions have to be set up to allow the measurement of the flow properties to be objective and reproducible. Isaac Newton was the first to express the basic law of viscometry, describing the flow behaviour of an ideal liquid.

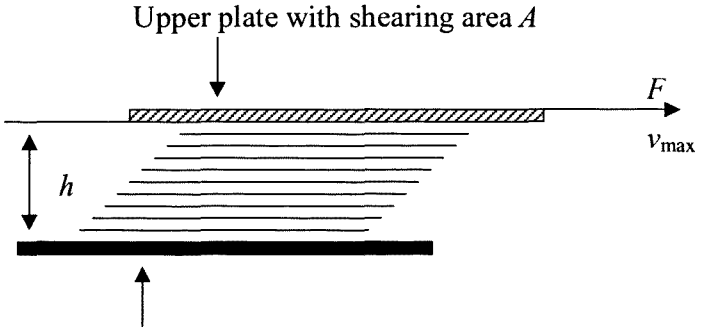


2.1

The simplest model by which to define the rheological parameters in equation 2.1 is the two-plate-Model (Scheme 2.1). A test sample is sheared between two plates, distance h apart. It is assumed that the sample has adhesion to the surfaces of both the plates. By application of a (shearing) force F, the upper plate with an (shearing) area A is moved at a speed v. The lower plate is fixed and immobile. A laminar flow of liquid layers (not a turbulent flow) occurs. This is required to calculate rheological parameters in a simple

way. The velocity of flow that can be maintained for a given force is controlled by the internal resistance of the liquid, i.e. by its viscosity.

Scheme 2.1: The two plate model.



Shear stress

A force F (units $N_{(Newton)}$) applied to an area A (units m^2), the interface between the upper plate and the liquid underneath, leads to a flow in the liquid layer. The shear stress τ (units Pa) is defined by equation 2.2.

$$\tau = \frac{F}{A} \qquad 2.2$$

Shear rate

The shear stress τ causes the liquid to flow in a special pattern (laminar flow). A maximum flow speed v_{max} is found at the upper boundary. The speed drops linearly across the gap, of distance h, to v_{min}= 0 at the lower boundary contacting the stationary plate. The speed drop across the gap between plates is named the "shear rate" (units s^{-1}) and in its general form it is defined by the following differential equation.

$$\dot{\gamma} = \frac{dv}{dh} \qquad 2.3$$

The speed difference between the neighbouring layers is the same (dv = constant) in a laminar ideal-viscous flow and all individual layers are accepted as equally thick (dh =

constant). In such a case, the shear rate $\dot{\gamma}$ is constant everywhere between these two plates.

Shear viscosity

In the "Principia", published in 1687, by Isaac Newton, there appeared the following hypothesis associated with the steady simple shearing flow shown in Scheme 2.1: "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another". This lack of slipperiness is what we now call "viscosity". Viscosity is synonymous with "internal friction" and is a measure of "resistance to flow". The shear stress τ is proportional to the shear rate $\dot{\gamma}$, i.e. if the applied force is doubled, the shear rate will be doubled. The constant of proportionality η (units Pa.s) is called the coefficient of viscosity.

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad 2.4$$

The parameters η and G (equation 2.11 in section 2.2.3.1) serve the same purpose of introducing a resistance factor linked mainly to the nature of the body being sheared.

2.2.2.2 Newtonian flow behaviour

The shear viscosity of Newtonian substances is independent of the shear load (shear stress). The mathematical description of this type of flow behaviour is given by equation 2.1. Examples of Newtonian substances include water, solvents, mineral oil (without polymer additives), glycerine, and blood plasma.

The shear viscosity is described by equation 2.4. The viscosity for such a substance is obtained from the slope of a plot of shear rate versus shear stress at any pair of points (τ, $\dot{\gamma}$) of the flow curve (Figure 2.1).

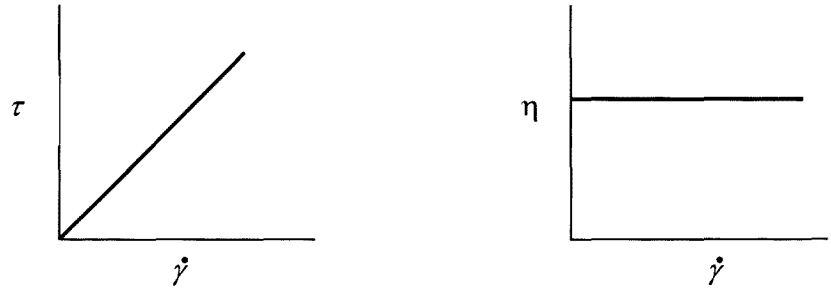
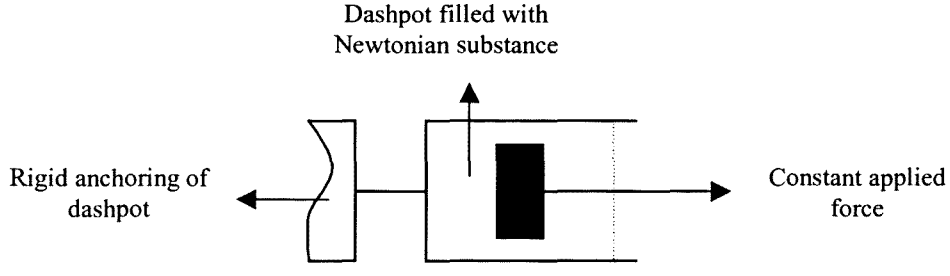


Figure 2.1: Flow curves and shear viscosity curves of Newtonian substances.

The mechanical model of a viscous substance (according to Newton) is the dashpot-model (Scheme 2.2). In this model, as long as an applied force acts on the piston, the test material in the damper is steadily deformed. If, however, the force is removed, the piston stays in the final position, and the deformed test substance remains irreversibly deformed after the shear load.

The entirety of the deformation energy acting on a viscous substance is lost as deformation work to the substance, and as resulting heat to the surroundings. This is an irreversible process, and the applied energy is no longer available for recovery after this process. The shear stress and deformation of an ideal Newtonian substance versus time is shown in Figure 2.2. The time interval t0 to t1 represents the loading phase and the time interval t1 to t2 represents the unloading interval. The units for the axis in Figure 2.2 are arbitrary.

Scheme 2.2: The dashpot-model according to Newton.



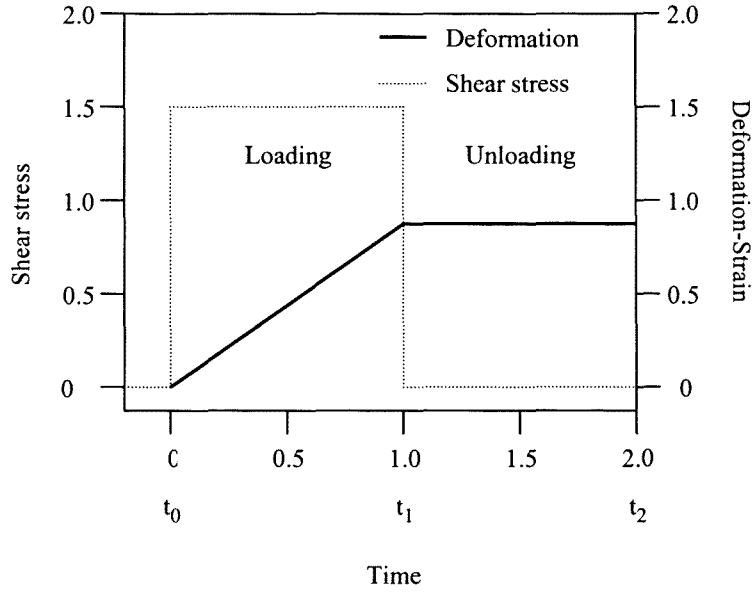


Figure 2.2: The shear stress and deformation of an ideal Newtonian substance versus time.

2.2.2.3 Non-Newtonian flow behaviour

Most viscous substances do not show Newtonian behaviour; those not exhibiting this ideal flow behaviour are called non-Newtonian substances.

Pseudoplastic flow behaviour

The shear viscosity of a substance with pseudoplastic flow behaviour depends on the shear load. In such a case, the shear viscosity decreases with increasing load. The terms "pseudoplastic" and "shear thinning" have the same meaning. Pseudoplastic test substances shows shear viscosity values that depend on the shear load. Since these values are not constant, the terminology "apparent shear viscosity" is used. Therefore, it is necessary to point out at which shear stress or shear rate the shear viscosity is determined. Figure 2.3 shows the flow curve and shear viscosity curve of pseudoplastic substances.

An empirical mathematical description of flow curve function for these fluids is given by W. Ostwald:[2]

$$\tau = K \dot{\gamma}^n \qquad 2.5$$

where K is the fluid "consistency index" and n is a power law index ($n < 1$).

The "Ostwald model" is also known as "Ostwald / de Waele model" or as the "power law model".

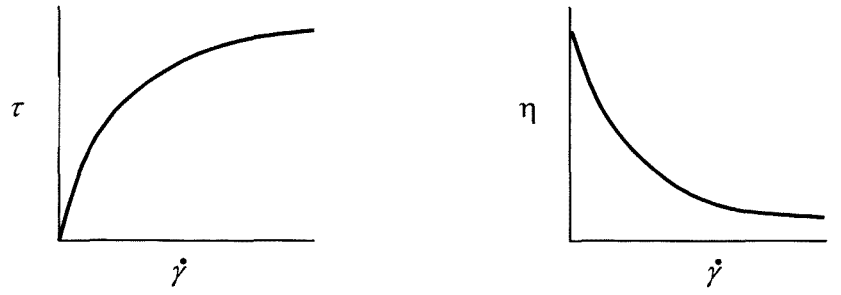


Figure 2.3: Flow curve and shear viscosity curve of a pseudoplastic substance.

Dilatant flow behaviour

The shear viscosity of a dilatant substance is dependent on the shear load, with the shear viscosity increasing with increasing load. The terms "dilatant" and "shear thickening" have the same meaning.

The flow curves for such fluids can also be described by equation 2.5, with a power law index, $n > 1$. Figure 2.4 shows the flow curve and shear viscosity curve of a dilatant substance.

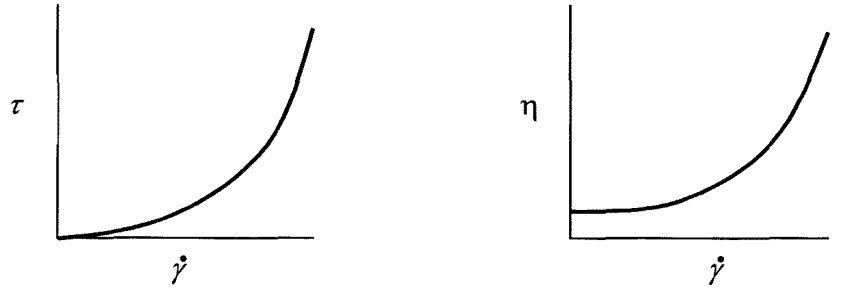


Figure 2.4: Flow curve and shear viscosity curve of a dilatant substance.

Plasticity

Plastic substances are described as pseudoplastic substances, which additionally feature a yield point. Materials with an apparent yield point (also called yield stress) are substances

that only begin to flow when the forces applied from outside (external forces, F_{ext}) are greater than the structural forces acting within the material (internal, F_{int}). Below the apparent yield point the material shows elastic properties, i.e. it behaves like a solid, where very small reversible deformations will be found after removal of the load.

Therefore, if $F_{ext} < F_{int}$, the substance is deformed only slightly (within the elastic range) and if $F_{ext} > F_{int}$, the substance shows viscous flow.

Typical substances showing yield points include oil well drilling muds, greases, lipstick masses, toothpastes and natural rubber polymers. Plastic liquids have flow curves that intercept the ordinate not at the origin, but at the yield point level τ_0 (Figure 2.5). A number of different models, for example the (a) Bingham,[3-5] (b) Casson,[6] and (c) Herschel-Bulkley [7] models, have been used to mathematically describe this type of flow behaviour (Figure 2.5).

(a) The mathematical description of the flow curve function with apparent yield point, according to Bingham:

$$\tau = \tau_0 + u_p \dot{\gamma} \qquad 2.6$$

with τ_0 being the Bingham yield point (yield stress) and u_p the Bingham viscosity.

(b) The mathematical description of the flow curve function with apparent yield point according to Casson:

$$\tau^{1/2} = \tau_0 + u_c \dot{\gamma}^{1/2} \qquad 2.7$$

with τ_0 being the Casson yield point (yield stress) and u_c the Casson viscosity.

(c) The mathematical description of the flow curve function with apparent yield point according to Herschel-Bulkley:

$$\tau = \tau_0 + u_h \dot{\gamma}^n \qquad 2.8$$

with τ_0 being the yield point (yield stress) according to Herschel-Bulkley and u_h the Herschel-Bulkley viscosity. For $n < 1$, pseudoplastic behaviour applies and for $n > 1$, dilatant behaviour applies.

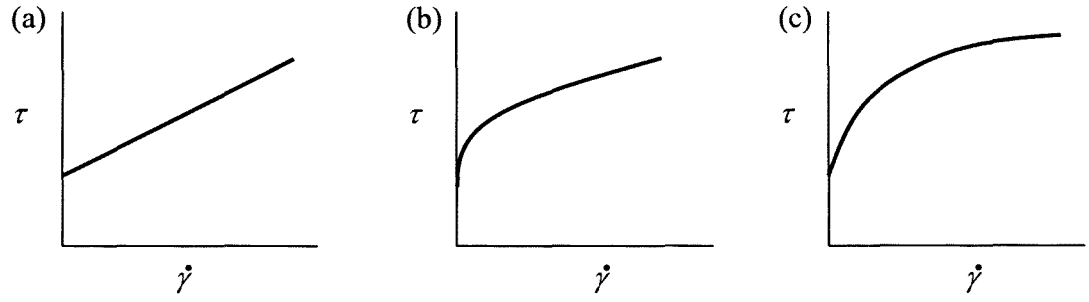


Figure 2.5: Different flow curves with yield points according to (a) Bingham, (b) Casson and (c) Herschel-Bulkley models.

Thixotropy

Thixotropic behaviour is characterised by reduction of the structural strength during the shear loading interval and structure recovery during the unloading interval. During the unloading interval the original structure recovers completely after a period of time. The time period for recovering to the original state during the unloading interval (t_B) is longer than the time period for reduction of the structural strength during the loading interval (t_A). This is a completely reversible process. Figure 2.6 shows the flow curve and Figure 2.7 shows the viscosity-time-curve of a thixotropic substance. Thixotropic behaviour is defined exclusively as time dependent behaviour.

Thixotropy is only determined in a scientifically correct way, if:

a) the viscosities in both intervals, i.e., the structure decomposition and structure recovery intervals, are measured, and

b) a constant shear load is applied in each measuring interval (as constant shear rate or as constant shear stress). In the loading interval, a high shear load, and in the unloading interval, an extremely small shear load, is preset for successful determination of the thixotropy of the substance.

This rheological phenomenon of thixotropy is of great industrial importance. Examples include almost all dispersions (suspensions, emulsions, foams), pastes, creams, ketchup and gels.

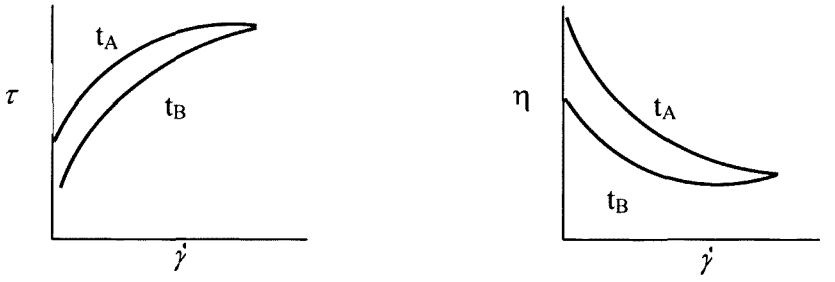


Figure 2.6: The flow curve of a thixotropic substance.

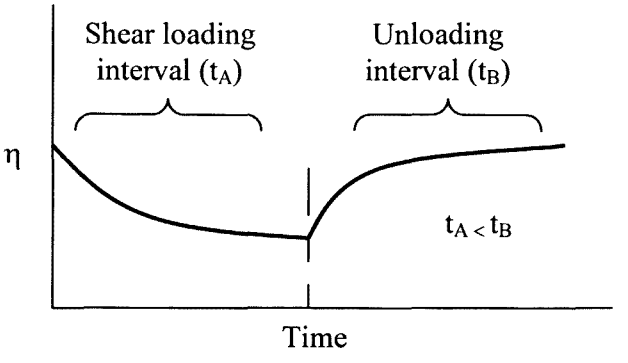


Figure 2.7: Viscosity curve of a thixotropic substance.

2.2.3 Deformation behaviour of elastic substances

The Two-Plate model is once again used to define rheological parameters (Scheme 2.3).

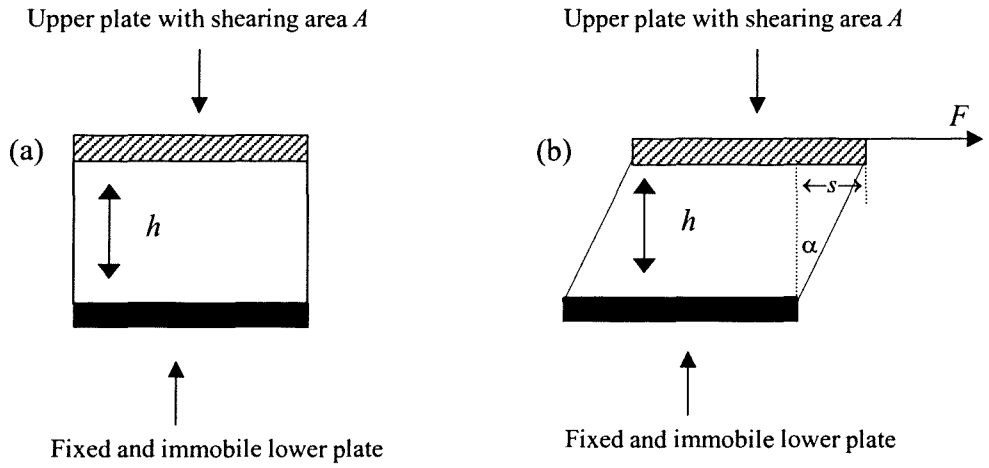
The measuring sample is sheared between two plates that have a distance h between them. For clarification, we consider a volume element of the measuring sample placed between the two plates and shaped like a cube with an edge length h. It is assumed that the sample has adhesion to both surfaces of the plates. By a (shearing) force F the upper

plate with an (shearing) area A is moved by a deflection of distance s. The lower plate is fixed and immobile.

Scheme 2.3: The Two-Plate model with a volume element of the measuring sample.

(a) unloaded, at rest

(b) deformed, under shear load



In the sheared state the volume element will be deformed. The shear deformation (shear strain) is defined by equation 2.9.

$$\gamma = \frac{s}{h} = \tan \alpha \qquad 2.9$$

with s [units m] being the deflection, h [units m] the plate distance and α [°] the deflection angle. The deformation is dimensionless.

2.2.3.1 Hookean deformation behaviour

Hookean deformation describes the behaviour of a purely elastic substance. Its behaviour is at the opposite end of the "behaviour scale" compared to that of a Newtonian

substance. Hooke's law is applied with shearing of an ideal elastic substance. The shear stress is directly proportional to shear deformation (shear strain) and does not depend on the rate of deformation i.e., if the applied force is doubled, the shear strain will double. The constant of proportionality G is called the shear modulus (Young's modulus). The Young's modulus in equation 2.10 is a correlating factor indicating stiffness, linked mainly to the chemical-physical nature of the solid substance involved. It defines the resistance of the solid against deformation.

$$\tau = G \cdot \gamma \qquad 2.10$$

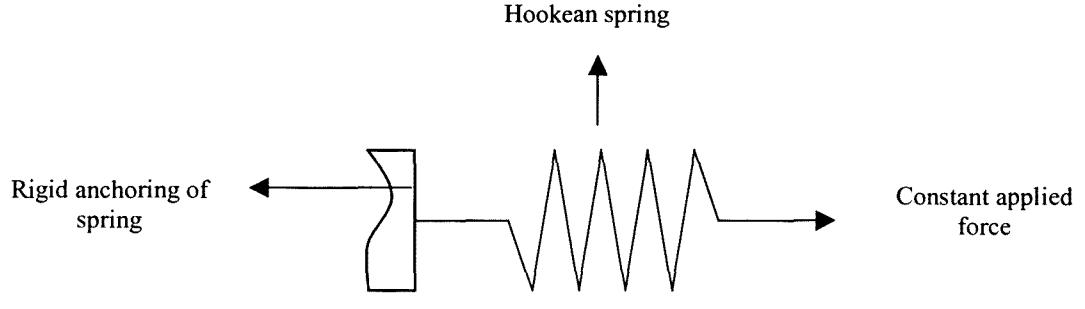
τ shear stress [Pa]

G shear modulus [Pa]

γ deformation [dimensionless]

Using the spring model (Scheme 2.4) it can be shown that under a constant applied force, a deformation of the body occurs without any time delay, corresponding to the stiffness of the substance. After removal of the applied force the substance moves back immediately with complete recovery to its original state. Figure 2.7 shows the shear stress and strain of an ideal solid versus time. There is no remaining deformation, unlike that observed for a Newtonian liquid (dashpot-model) (Section 2.2.2.1). The time interval t_0 to t_1 represents the loading phase and the time interval t_1 to t_2 represents the unloading interval. The units for the axis in Figure 2.8 are arbitrary.

Scheme 2.4: The spring model according to Hooke.



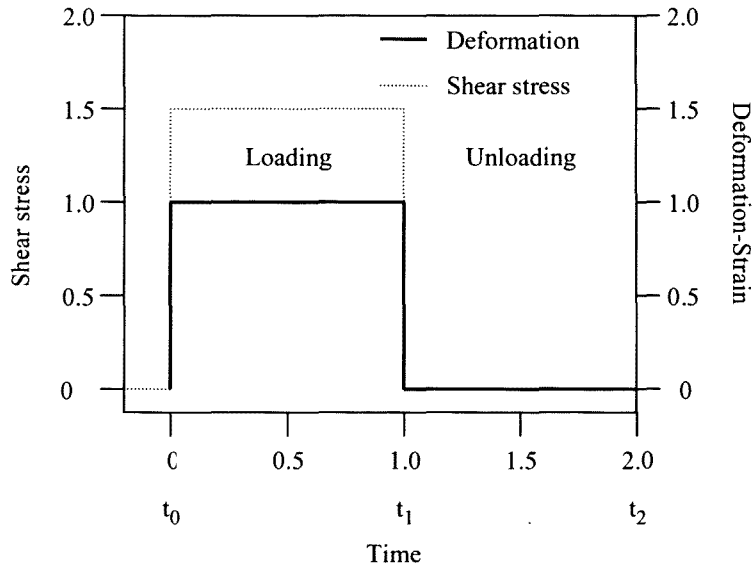


Figure 2.8: The shear stress and strain of an ideal solid versus time.

2.2.4 Deformation behaviour of viscoelastic substances

A viscoelastic substance shows viscous and elastic behaviour. It is important to distinguish between viscoelastic liquids and viscoelastic solids because of their different deformation behaviours. The Maxwell model and Kelvin-Voigt model are described in the following section and are used to distinguish between these two different deformation behaviours.

2.2.4.1 Maxwell liquid (viscoelastic liquid)

The elastic portion of a viscoelastic liquid behaves according to Hooke's law (spring model) and the viscous portion behaves according to Newton's law (dashpot model). A model can show the behaviour of viscoelastic liquids as a combination of the spring and the dashpot in a serial connection. This model was presented in the year 1866 by the physicist James C. Maxwell and is called the "Maxwell model" (Scheme 2.5).

Scheme 2.5: The Maxwell model describes a viscoelastic liquid as a combination of a spring and a dashpot in a serial connection.

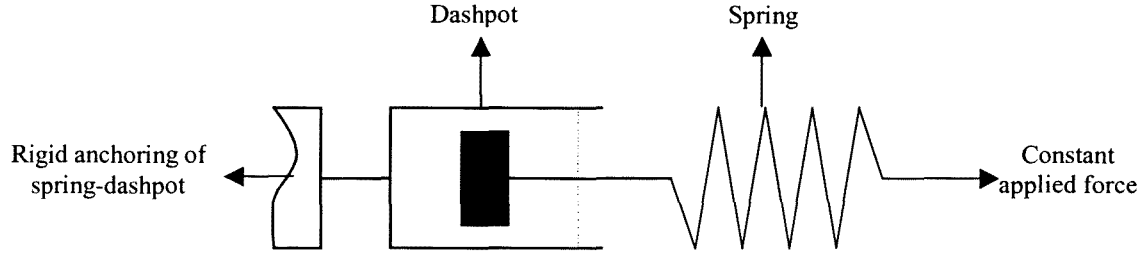


Figure 2.9 shows the creep and recovery of Maxwell liquid versus time. The creep and recovery method allows one to differentiate between the viscous and the elastic responses of a test substance. In comparison to normal force measurement, which marks the shear rate dependency of viscosity and elasticity, the creep and recovery measurement introduces the additional parameter of "response time" to the stress-dependency of both viscous and the elastic behaviour of solids and liquids. The time interval t_0 to t_1 represents the loading phase and the time interval t_1 to t_2 represents the unloading interval. The units for the axis in Figure 2.9 are arbitrary.

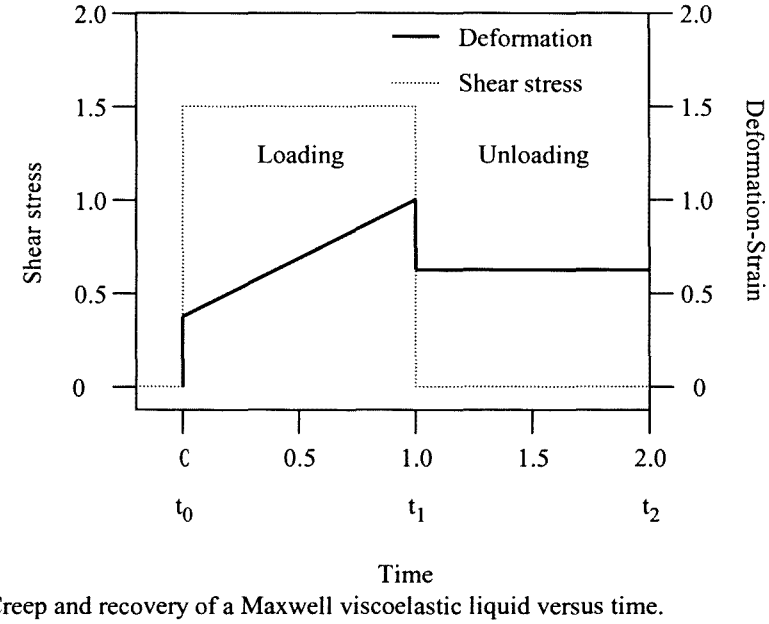


Figure 2.9: Creep and recovery of a Maxwell viscoelastic liquid versus time.

Loading (t_0 to t_1):

The substance under stress immediately shows a deformation of the elastic component with an instantaneous step of strain increase in accordance to the elastic response of the spring. The viscous component (modelled by the dashpot) however, under this acting load, continues to be deformed irreversibly. As a result the deformation-time function (γ - *t*) (Figure 2.9) shows a sudden increase in γ, followed by a straight line with a constant slope.

Unloading (t_1 to t_2)**:**

When the applied stress is instantaneously removed at the time t_1, the strain drops immediately to a new time-constant level. This drop relates to the stress release of the spring while the remaining permanent strain is equivalent to the amount of the viscous flow during the loading phase. As a result the deformation-time function (Figure 2.9) after the force is removed shows a sudden decrease in γ, followed by a straight line with a constant value.

After loading and following unloading, the substance remains partially deformed. Total recovery from deformation does not take place. With this kind of behaviour, the test substance is characterised as a viscoelastic liquid.

The Maxwell model is mathematically defined as follows:

Assumption 1:

The total deformation is the sum of the two single deformations of the two elements:

$$\gamma = \gamma_v + \gamma_e \qquad 2.11$$

The same applies for the shear rates:

$$\dot{\gamma} = \dot{\gamma}_v + \dot{\gamma}_e \qquad 2.12$$

$$\text{with } \dot{\gamma} = \frac{d\gamma}{dt}$$

Assumption 2:

The same shear stress is acting on each of the two elements:

$$\tau = \tau_v = \tau_e \qquad 2.13$$

For the viscous element (dashpot) Newton's formula applies:

$$\eta = \frac{\tau_v}{\dot{\gamma}_v} \qquad \text{or} \qquad \dot{\gamma} = \frac{\tau_v}{\eta}$$

For the elastic element (spring) Hooke's formula applies:

$$G = \frac{\tau_e}{\gamma_e} \qquad \text{or} \qquad \gamma_e = \frac{\tau_e}{G} \qquad \text{or} \qquad \dot{\gamma}_e = \frac{\dot{\tau}}{G}$$

with $\dot{\tau} = \frac{d\tau}{dt}$ change (derivative) of the shear stress with respect to time [Pa.s]

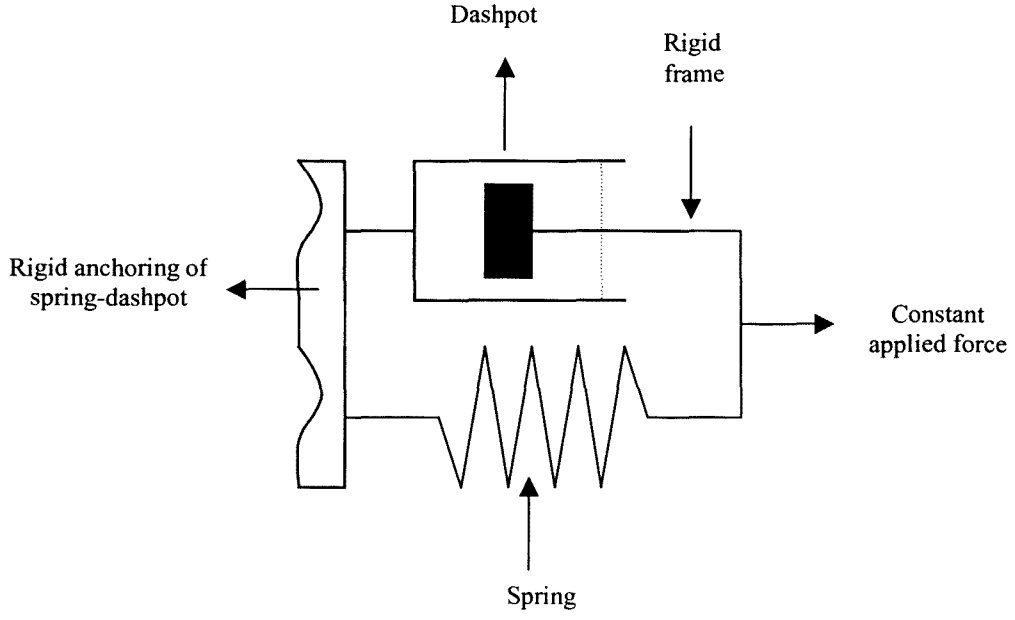
Thus, using Maxwell's model for the total shear rates, the following differential equation is obtained:

$$\dot{\gamma} = \dot{\gamma}_v + \dot{\gamma}_e = \frac{\tau}{\eta} + \frac{\dot{\tau}}{G} \qquad 2.14$$

2.2.4.2 Kelvin-Voigt solid (viscoelastic solid)

The behaviour of a viscoelastic solid can be modelled as a combination of a spring and a dashpot in a parallel connection. A rigid frame connects the two components. William T. Kelvin and Voigt presented this model in the year 1890. It is called the "Kelvin-Voigt model" (Scheme 2.6). The time interval t_0 to t_1 represents the loading phase and the time interval t_1 to t_2 represents the unloading interval. The units for the axis in Figure 2.10 are arbitrary.

Scheme 2.6: The Kelvin-Voigt model describes a viscoelastic solid as a combination of a spring and a dashpot in a parallel connection.



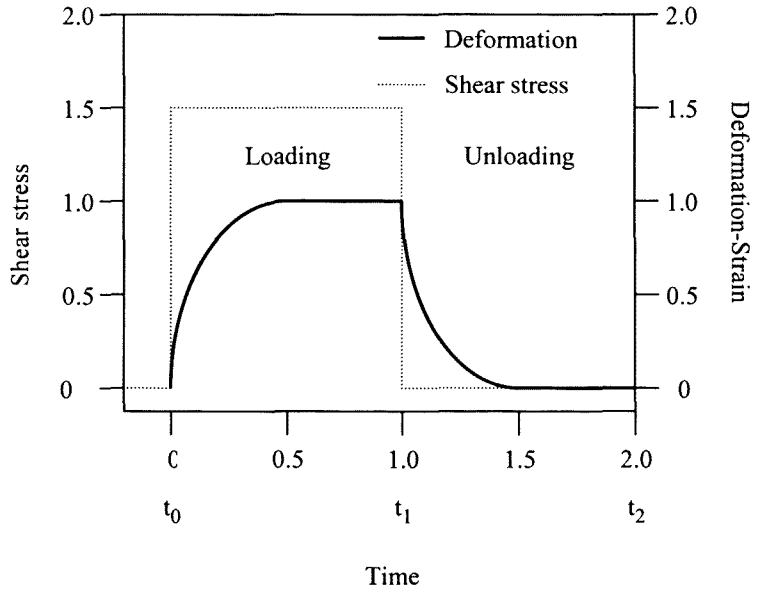


Figure 2.10: Creep and recovery of a Kelvin-Voigt viscoelastic solid versus time.

Loading (t_0 to t_1):

Deformation of the two connected elements takes place as long as the constant loading force is acting. The elastic portion (spring) cannot be deformed in such a spontaneous way as would happen if it were present as a solitary component, because it is braked by the viscous portion (dashpot). As a result, the deformation behaviour will be a time dependent function, which can be presented in a deformation - time diagram (Figure 2.10) as an exponential function with increasing γ values.

Unloading(t_1 to t_2):

Finally, with a time delay caused by the dashpot, the original state without any remaining deformation will be obtained at some time after the applied force is removed. Both the deformation and recovery are reversible processes. Therefore, a complete recovery to the original state takes place and, due to this behaviour, the test substance is classified as a viscoelastic solid. This behaviour is in contrast to that of a Maxwell viscoelastic liquid that remains partially deformed after the unloading phase. As a result the deformation behaviour shows a time-dependent function, which can be presented in a deformation – time diagram (Figure 2.10) as an exponential function with decreasing γ values.

The Kelvin-Voigt model is mathematically defined as follows:

Assumption 1:

The acting total shear stress applied is equal to the sum of the stresses in the dashpot τ_v and the spring τ_e:

$$\tau = \tau_v + \tau_e \qquad 2.15$$

Assumption 2:

The deformation or shear rate of both elements is the same:

$$\gamma = \gamma_v = \gamma_e \qquad \text{or} \qquad \dot{\gamma} = \dot{\gamma}_v = \dot{\gamma}_e \qquad 2.16$$

with $\dot{\gamma} = \frac{d\gamma}{dt}$ change (derivative) of the deformation with respect to time = shear rate.

For the viscous element (dashpot) Newton's formula applies:

$$\tau_v = \eta \cdot \dot{\gamma}_v \qquad 2.17$$

For the elastic element (spring) Hooke's formula applies:

$$\tau_e = G \cdot \gamma_e$$

Thus, using Kelvin-Voigt's model for the total shear stress, the following differential equation is obtained:

$$\tau = \tau_v + \tau_e = \eta \cdot \dot{\gamma} + G \cdot \gamma \qquad 2.18$$

The Maxwell model and Kelvin–Voigt model are relatively simple inasmuch as they only link a single dashpot with a single spring. These models successfully define the concept of viscoelastic behaviour, whether one deals with a viscoelastic solid (Kelvin-Voigt solid) or a viscoelastic liquid (Maxwell liquid). Real viscoelastic substances are represented by more complex combinations of springs and dashpots and will not be discussed in this section.

2.3 Thickeners/Rheology modifiers

2.3.1 Introduction

Alkali-soluble polymers, especially hydrophobically modified polymers, are extensively used as thickeners and rheology modifiers in a variety of products. Extensive research efforts have been devoted to studying their interactions in aqueous and emulsion systems, with the goal of better understanding their structure/property relationships.[8-10] In the paint and coating industry, water-based paints are fast replacing the conventional solvent-based varieties due to increasingly stringent environmental regulations. These water-based paints usually require adjustment of their rheology profile to give high application performance. A rheology profile describes the shear rate and time dependent paint viscosity that affects such properties: as pigment settling, brush and roller pickup, film build, levelling and sagging of the film on vertical surfaces.[11-15]

It is possible to have limited control over the viscosity by varying the concentration of the latex and other solids dispersed in the formulation. It is not until high volume fractions are reached that the dispersed phase contributes significantly to the viscosity and, because the viscosity rises very steeply in this region, it is very difficult to achieve fine control of the viscosity of a latex-based formulation. By manipulating particle size and absorbed material it is possible to control the effective volume fraction of solids to some extent. This however often fails to meet the needs of the formulator, and often involves compromise of other performance properties. Increasing viscosity by increasing the volume fraction of solids is usually the most expensive route to follow, especially in the case of latex-rich formulations.

Water-soluble polymers give the formulator a much more efficient and controllable tool for adjusting viscosity. The viscosity and rheology are not only functions of the concentration of polymer, but also of its molar mass, the flexibility of its molecular coil, and the charges on the polymer in solution. There are two different ways that are conventionally used to represent the efficiency of water-soluble polymers in controlling and adjusting viscosity. The first way is to express the thickening efficiency in terms of the viscosity obtained for a given concentration of the water-soluble polymer. The second

way is expressed in terms of the amount of alkali-soluble polymer required to obtain a specific viscosity in a latex formulation.

Cost is only one reason why thickening efficiency is of concern to coating manufacturers. A key property of most water-based coatings formulations is their ability to resist water once a film is formed. The introduction of water-soluble polymers will inevitably compromise this performance to some extent and it is therefore important to use only as much thickener as is necessary to achieve the desired viscosity and rheology.[16, 17] The formulator is often faced with difficult choices in that the most efficient thickeners are not always the best for providing the overall rheology profile necessary for a given application. The formulator must often use a combination of different thickeners (different thickener structures) to acquire the desired low and high shear viscosities.

2.3.2 Classification of thickeners/rheology modifiers

Paint thickeners/rheology modifiers can be classified in several ways, according to whether they are organic or inorganic, soluble or swellable, naturally derived or completely synthetic, nonionic or anionic and associative or non-associative. Associative thickeners are also referred to as rheology modifiers. Table 2.1 gives the classification of different types of thickeners/rheology modifiers.

Table 2.1: Classification of the different types of thickeners/rheology modifiers.

ORGANIC THICKENERS

NON-ASSOCIATIVE

Naturally derived

Nonionic cellulosics, e.g., hydroxyethyl cellulose, methyl cellulose, ethyl hydroxyethyl cellulose, hydroxypropyl cellulose

Anionic cellulosics, e.g., carboxymethyl cellulose

Other polysaccharides, e.g., dextran, alginates

Other, e.g., caseinates

Synthetic

Nonionic, e.g., polyethylene oxide, polyvinyl alcohol, polyacrylamide, ethylene-oxide based polyurethanes

Alkali-soluble, e.g., acrylics, styrene/maleic anhydride

Alkali swellable, e.g., cross-linked acrylic acid emulsions

ASSOCIATIVE

Naturally derived

Nonionic

Hydrophobically modified hydroxyethyl cellulose (HMHEC)

Synthetic

Nonionic

Hydrophobically modified ethylene oxide urethane (HEUR)

Hydrophobically modified polyacrylamide (HPAM)

Anionic

Hydrophobically modified alkali soluble (or swellable) emulsion (HASE)

INORGANIC THICKENERS

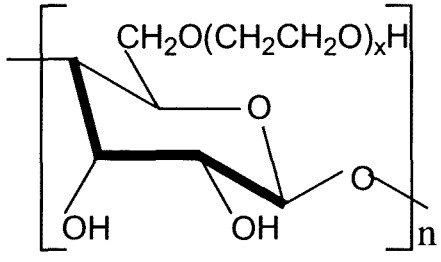
Clays, e.g., attapulgite, bentonite

Titanium chelates

2.3.3 Cellulose thickeners

The best-known non-associative thickeners are those derived from cellulose. These water-phase thickeners have been successfully used in the paint industry for many years.[18-20] Cellulose itself is a naturally occurring polysaccharide consisting of repeating anhydroglucose units, which provide a relatively straight and stiff polymeric backbone. The inflexible polymer backbone causes these thickeners to occupy a large volume in the water phase, therefore cellulose is very effective in increasing the viscosity of water. Hydroxyethyl cellulose (HEC) is the most common cellulose thickener used in paints, but there are also others, such as methyl cellulose, hydroxypropylmethyl cellulose, and ethylhydroxyethyl cellulose. The chemical structure of HEC is given in Scheme 2.7.

Scheme 2.7: The chemical structure of hydroxy ethyl cellulose (HEC).

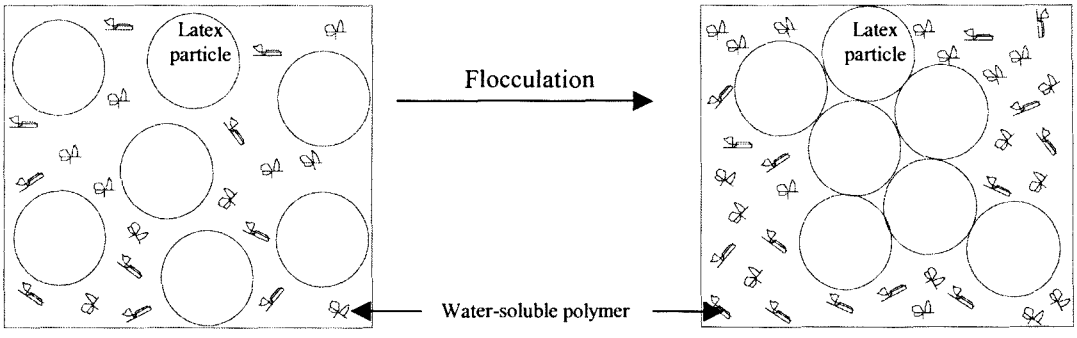


Although cellulose thickeners have been used in the latex paint industry for many years they have been unable to provide latex paints with the application and appearance properties of solvent-based alkyd paints. These products (cellulose thickeners) tend to impart a higher low shear viscosity than is sometimes desirable, which impedes the leveling of brush marks, and a lower high shear viscosity which limits film build up that is important for both hiding and protection of the substrate.

Modern high performance emulsions tend to have smaller particle sizes, and in paints formulated on such binders, cellulose thickeners have a strong tendency to flocculate the polymer. It has been shown that in most practical latex products, such as paints, the adsorption tendency of cellulose thickeners is relatively weak, and they are easily displaced by surfactants present in virtually all latices and their formulations. Thus, the soluble polymer is in fact "free" in the aqueous phase, and this can lead to flocculation and/or phase separation of the latex, in this case by a process known as volume restriction

flocculation.[21-23] The mechanism for volume restriction flocculation is shown in Scheme 2.8. When latex particles in the presence of non-adsorbing water-soluble polymers, such as the common grades of cellulose ethers, approach each other so that the interparticle spacing is less than the coil diameter of the soluble polymer, the soluble polymer is excluded from the interparticle region, resulting in a lower local polymer concentration. There is thus an osmotic pressure imbalance that tends to force the latex particles together. The characteristics of the resulting flocs depend on the particle size and volume fraction of the latex and on the concentration of the water-soluble polymers. Volume restriction flocculation hinders gloss development.

Scheme 2.8: The mechanism for volume restriction flocculation.

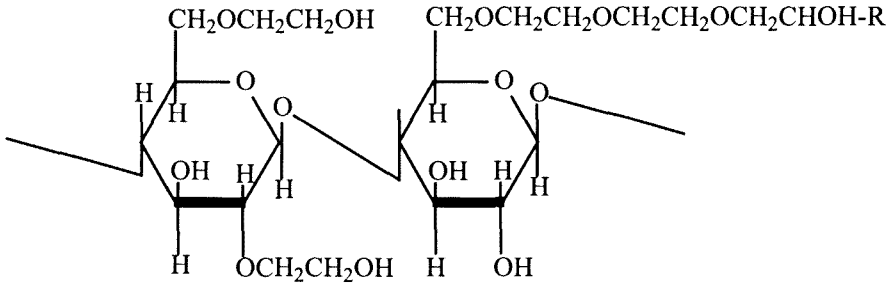


By altering the molar mass, different grades of cellulose thickeners have been developed. Higher molar mass derivatives have excellent thickening efficiency, but tend to be more pseudoplastic because shearing forces break down molecular chain entanglements. If sufficient levels are used to achieve adequately high shear viscosity, then low shear viscosity is too high. High molar mass cellulose thickeners also tend to cause paints to spatter excessively, especially when applied by roller. The low molar mass cellulose thickeners, on the other hand, are less pseudoplastic in nature, but need to be used at much higher levels to give adequate viscosity. Water sensitivity and cost then become important issues. Therefore, grades of intermediate molar mass have been more traditionally used. Like other naturally derived thickeners, they are also prone to enzymatic degradation, and therefore lead to a decrease in viscosity of the paint during storage.[24, 25]

Cellulose thickeners can also be hydrophobically modified. This gives them (those of lower molar mass) the same thickening efficiency as much higher molar mass grades of

normal HEC thickeners. A schematic representation of a hydrophobically modified hydroxylethyl cellulose (HMHEC) molecule is shown in Scheme 2.9. HMHEC appears to associate very little with latex particles themselves, interacting more strongly with pigments and extenders, and with the dispersants and surfactants used to stabilise them.[26]

Scheme 2.9: Schematic representation of an HMHEC molecule.



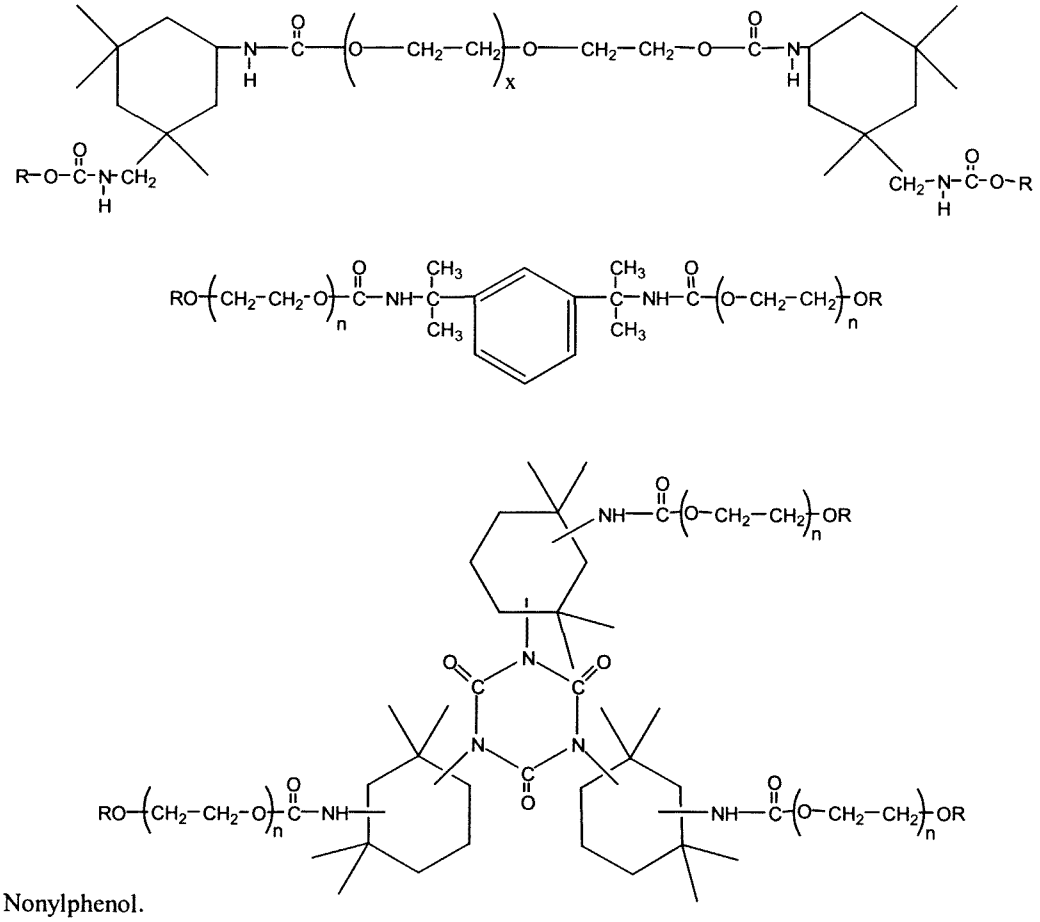
R represents a hydrophobic alkyl group.

2.3.4 Hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers

In comparison with cellulose associative thickeners, HEUR rheology modifiers have relatively low molar masses. They are composed of condensation products of polyethylene glycol and diisocyanates, which are capped with hydrophobic groups. The wide variety in the structure of the individual components allows the synthesis of HEUR rheology modifiers with very different compositions and thus varying degrees of effectiveness. For example, the performance of the thickeners in latex formulations can be fine-tuned by adjusting the hydrophobic blocks in the polymer chain, e.g. by varying the hydrophobe carbon content using diisocyanates of diverse hydrophobicity. The use of polyisocyanates and a variety of poly(ethylene oxide)diols can produce branched or star shaped structures. Scheme 2.10 shows some examples of different types of HEUR rheology modifiers. Molar masses of the order of 40 000 to 50 000 are typical. Because of their relatively low molar mass and the high flexibility of their backbone, almost all of the thickening power comes from association.[27,28] The hydrophobic groups associate with the emulsion particles through adsorption onto the particle surface.[29] In addition, they aggregate in the water phase in a similar way to that in which surfactants form micelles.

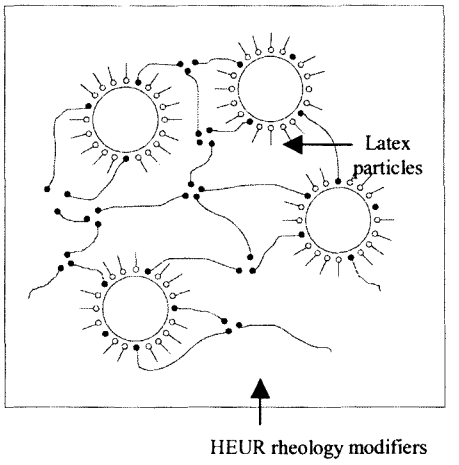
This network formation results in a large increase in viscosity. A schematic representation of the network formation is given in Scheme 2.11. To provide efficient network formation, the molar mass of the poly(ethylene oxide) backbone of the rheology modifiers must be sufficiently high, but not too high to dilute the effectiveness of the hydrophobic clusters.[30-32] The placement of the hydrophobic groups may have a small influence on the surface-active behaviour, but the size and number of hydrophobes are the major determinants of their performance properties.[32, 33]

Scheme 2.10: Examples of different types of HEUR rheology modifiers.



R= Nonylphenol.

Scheme 2.11: Network formation of HEUR rheology modifiers.



2.3.5 Alkali-swellable and alkali-soluble thickeners/rheology modifiers (ASTs)

These thickeners are defined as carboxyl functional copolymers produced by the free radical polymerisation of ethylenically unsaturated monomers. At low pH values the copolymers are substantially insoluble in water, but at higher degrees of ionisation they exhibit thickening on swelling or dissolution in aqueous media. In their ionic form (partially or fully neutralized), ASTs generally belong to the broad classes of aqueous polymers known as water-swellable or water-soluble polymers (WSPs) and hydrophobically modified water-swellable or water-soluble polymers (HWSPs).

ASTs have the distinction, however, of being anionic (neutral on preparation, but can be easily ionised because of the carboxyl functionality) and normally water insoluble on preparation and prior to final end-use application. This distinction has permitted a variety of synthetic techniques for their preparation, including solution polymerisation in organic solvent, precipitation polymerisation in organic diluent, aqueous suspension polymerisation, or, more commonly and most advantageously, aqueous emulsion polymerisation. Because of their performance characteristics and convenient handling (particularly the emulsions), ASTs find wide industrial applications in latex paints, carpet backing, adhesives, paper coatings, print pastes, agrochemical products, personal care products, household and industrial cleaners, and in oil field drilling-recovery operations.

2.3.5.1 Classification by chemical composition

The two main structural groups into which ASTs are generally classified are either "conventional" (those lacking associative functionality) or "associative". The structural distinction is usually supported by the contrast in their observed rheological properties. Conventional and associative ASTs have been synthesised by the copolymerisation of a broad variety of ethylenically unsaturated monomers. A least one of the monomers must have carboxyl functionality and be present in sufficient concentration to render the polymer water-swellable or water-soluble on partial or complete neutralisation with an appropriate base.

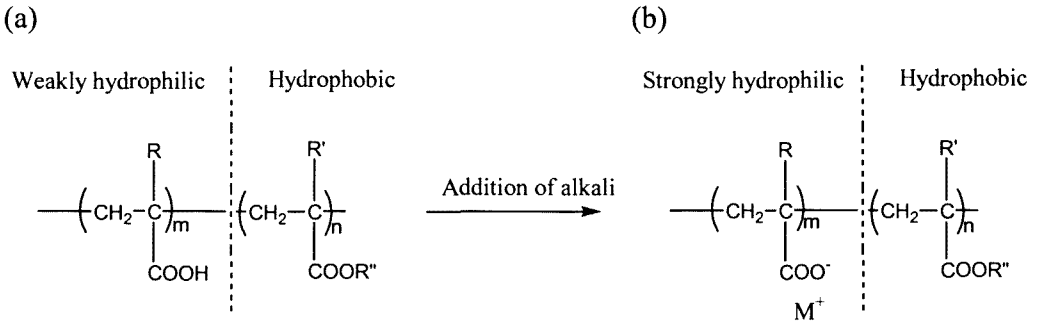
Monomers such as acrylic acid, methacrylic acid, itaconic acid, citraconic acid, maleic acid, fumaric acid, crotonic acid, maleic anhydride, and citraconic anhydride are among the carboxylic and anhydride functional monomers that have been used in the synthesis of these polymeric thickeners. Conventional ASTs are normally made up of only two types of monomers and are presumed to lack associative properties. In addition to the more hydrophilic carboxyl-containing acid monomers previously mentioned, conventional ASTs must contain one or more hydrophobic comonomers to obtain water-insolubility at low pH. By selecting a suitable ratio of the hydrophilic to hydrophobic components, it is possible to prepare polymers that are water insoluble in the free acid state as synthesised, but which become water-swellable or water-soluble when neutralised with alkali (e.g. hydroxides of monovalent cations and amines or amine derivatives). This behaviour is summarised in Scheme 2.12.

Scheme 2.12: A schematic representation of the neutralisation of water-swellable or water-soluble polymer by an appropriate alkali.

(a) Carboxylated polymer in free acid form (pH < 6). The polymer is water insoluble.

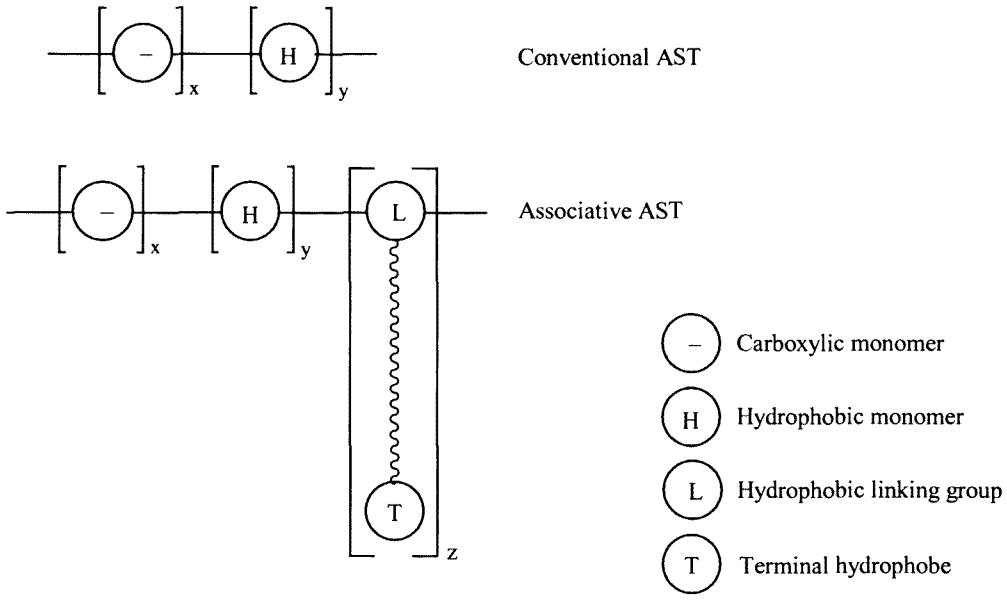
(b) Carboxylated polymer in ionised form (pH > 7). The polymer is water-soluble.

R and R' are H or CH_3. R" is alkyl (e.g. CH_3, C_4H_9)



Conventional ASTs are modified with macromonomers containing ethylene oxide and terminal hydrophobic functionality to produce associative ASTs. These associative ASTs and nonionic associative polymers (HEUR rheology modifiers) represent a significant advance in thickener technology, by conferring higher degrees of thickening or unique rheological properties to aqueous solutions and aqueous media containing dispersed-phase components. The advantages and disadvantages of the use of associative thickeners in general[34] and their influence on coating performances have been assessed.[35-38] Associative ASTs are usually terpolymers consisting of a carboxylic monomer, hydrophobic monomer, and a third macromonomer that is associative. They are prepared by the same polymerisation procedures used for conventional ASTs. In Scheme 2.13 a schematic representation of an associative AST is compared with that of a conventional AST.

Scheme 2.13: Schematic representation of a conventional vs. associative AST.



The associative monomers used to prepare associative ASTs most frequently contain a long chain hydrophilic segment terminated with a hydrophobic group. The hydrophilic segment usually consists of polyethoxylated or poly(ethoxylated-propoxylated) components situated between the ethylenic unsaturation at one end of the molecule and the terminal hydrophobic group at the other end. In one common mode of synthesis, the associative macromonomers are conveniently prepared by coupling the hydroxyl end group of a conventional nonionic surfactant with a monomer containing a polymerisable ethylenic unsaturation. Variability within the macromonomer structure is obtained by altering the type of terminal hydrophobe, type of ethylenic unsaturation, and size of the polyethoxylated or poly(ethoxylated-propoxylated) component.

2.3.5.2 Thickening mechanism of conventional ASTs

The thickening process during neutralisation of acid-group-containing linear copolymers in aqueous media is a well-known phenomenon. Verbrugge concluded that a single mechanism explains this process.[39] The proposed mechanism is that polymer molecules

become hydrated as the pH is raised and the carboxyl groups become charged (anions). This leads to expansion of the molecular coils because of the electrostatic repulsion of the carboxylanion charge centres, and results in dissolution and an increase in the polymer's hydrodynamic dimensions, which in turn increases intermolecular entanglement and the resistance to flow. This thickening process is referred to as hydrodynamic thickening (Scheme 2.14).[40]

Scheme 2.14: Hydrodynamic thickening mechanism of a conventional alkali-soluble polymer.

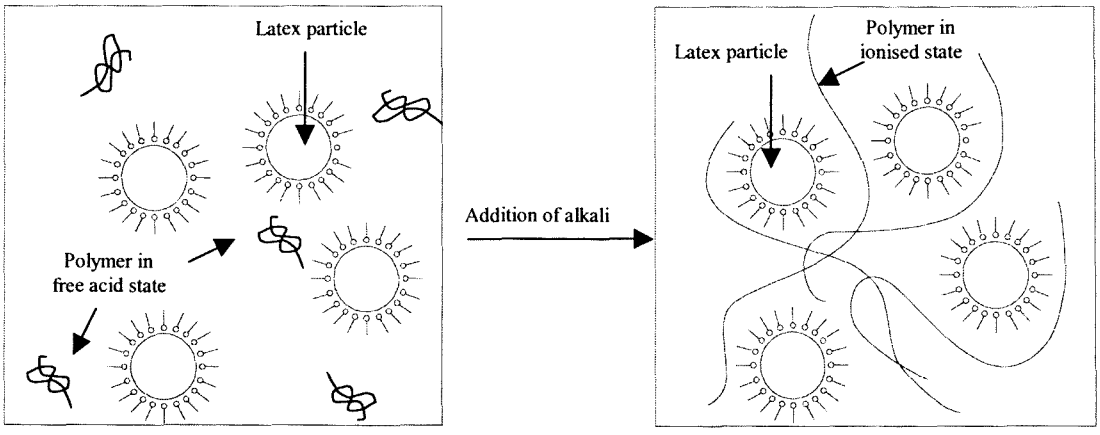


Table 2.2 lists a number of factors known to affect the thickening, swelling, or dissolution behaviour of conventional AST polymers.

Table 2.2: Factors known to affect the thickening, swelling, or dissolution behaviour of conventional AST polymers.

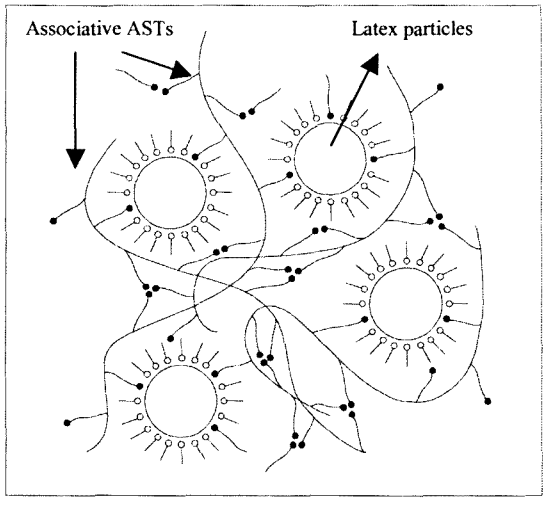
Type of carboxylic monomer.[41,42]
Level of carboxylic monomer.[41,42]
Hydrophilicity of the hydrophobic monomer.[41,42]
Glass transition temperature of the hydrophobic monomer. [43]
Polymer chain architecture (This will be shown in Chapters 3 and 4).[44]
Degree of polymerisation (This will be shown in Chapter 4).[44,45]
Degree of cross-linking.[39]
Degree of neutralisation.[46]
Polymerisation procedure.[47]
Emulsion particle size.[48]

2.3.5.3 Thickening mechanism of associative ASTs

Hydrophobically modified alkali-soluble polymers thicken by means of a dual mechanism: hydrodynamically (carboxyl content) and associatively (hydrophobe content). Because the hydrodynamic component of thickening is present for both conventional and associative ASTs, it is the associative mechanism that is responsible for the enhanced thickening and unique rheological properties frequently observed in aqueous solutions and dispersed-phase systems containing these thickeners. The associative mechanism can generally be described as a result of non-specific hydrophobic association of water-insoluble groups in water-soluble polymers.[49,50] The main interactive components for the associative alkali-soluble polymers are the terminal hydrophobic groups of the ethoxylated side chains.[51] The interaction of the hydrophobes can be either intramolecular (with other hydrophobic groups on the same polymer chain) or intermolecular (with other dispersed-phase particles and hydrophobic groups on other polymer chains) association. The association with other dispersed-phase particles, such as

latex particles, has been shown to be surface adsorption.[52] The building of structure within the aqueous phase and the interaction with particle surfaces in dispersed-phase systems gives the associative component a dual character (see Scheme 2.15).

Scheme 2.15: The dual thickening mechanism of associative ASTs.



Structurally, the backbone of an associative AST copolymer is predominantly hydrophilic because it contains sufficient carboxyl anions to render it water-soluble at elevated pH. The ethoxylated side chains attached to the backbone are also hydrophilic and, thus, the interior of the molecule is expected to be highly hydrated. The hydrophobes at the end of the ethoxylated side chains would, hypothetically, be repelled from this environment and at the same time be attracted to other terminal hydrophobic groups or hydrophobic surfaces if present. Like surfactants, the driving force for association is a result of the entropy gained by loss of water structuring around the hydrophobic groups and a minimisation of the water-hydrophobic group contact.[53]

The hydrodynamic thickening mechanism of conventional ASTs is also present in the associative ASTs. Factors affecting the thickening behaviour of both types of thickeners are therefore expected, and are indeed observed. The factors that affect the thickening efficiency of conventional ASTs listed in Table 2.2 are also applicable to associative ASTs. Table 2.3 contains a list of additional factors that affect the thickening efficiency or rheological properties of associative ASTs.

Table 2.3: Additional factors, to those tabulated in Table 2.2, that effect the thickening efficiency or rheology of associative ASTs.

Type of terminal hydrophobe.* [51]
Length of terminal hydrophobe.* [54]
Size of the polyethoxylated or poly(ethoxylated-propoxylated) component.[55]
Type of linking functionality.* [39]
Relative amount of associative monomer.[56]
Presence of water-soluble solvents, salts, and surfactants.[57, 58]
Presence of dispersed hydrophobic particles.[59]

* In the associative macromonomer

2.4 Controlled/Living free radical polymerisation – The RAFT process

2.4.1 Introduction

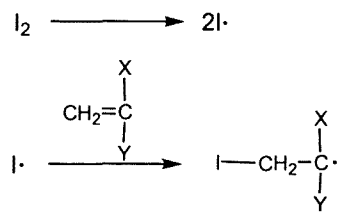
Conventional free radical polymerisation is one of the most convenient ways used by industry to manufacture a vast range of commercial polymer products. The popularity of the process stems from the fact that it can be carried out under relatively undemanding conditions. The tolerance of the process towards small amounts of impurities like stabilizers, oxygen and water makes it possible to synthesise high molar mass polymers without removal of the stabilisers in commercial monomers, in the presence of trace amounts of oxygen and in solvents that have not been rigorously dried.[60] Other attractive characteristics are its compatibility with a wide range of monomers and solvent systems. One of the most important attributes of radical polymerisation is that it can be conveniently conducted in aqueous media in the form of emulsion polymerisation.[61]

The major limitation of conventional free radical polymerisation is that it is difficult to attain control over the polymer structure. Broad molar mass distributions are generally observed and can only be crudely influenced by variation in the initiator concentrations and the use of chain transfer agents. The process has poor control over the chain architecture and end group functionalities of the polymers synthesised. The limitations are innate to the mechanism of conventional free radical polymerisation, primarily due to the relatively short lifetimes of growing chains with respect to total reaction time, which is primarily a result of extensive chain termination (Scheme 2.16).

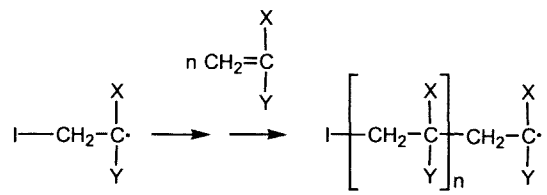
Initiation in polymerisation can be defined as the series of reactions beginning with the generation of primary radicals and culminating in addition to the carbon-carbon double bond of the monomer, to form initiating radicals. Initiation is followed by the propagation step of radical polymerisation, comprising a sequence of radical additions to carbon-carbon double bonds forming propagating radicals. These propagating radicals react with each other (the termination step) at or near diffusion-controlled rates, giving rise to "dead" polymer chains. Termination is a bimolecular reaction, shown by Benson and North[62] to involve a three-step process. The reason is that the encounter step of termination is a two-step event where the radicals must first meet and then, secondly, the actual free-radical sites must find each other. Therefore termination involves chain encounter, then chain-end encounter, and finally chemical reaction itself. The encounter steps that involve the motion of large polymeric species are relatively slow in comparison with the actual chemical reaction step, which is fast. The self-reaction of the propagating radicals is by combination and/or disproportionation.

Scheme 2.16: Simplified schematic representation of the conventional free radical polymerisation mechanism.

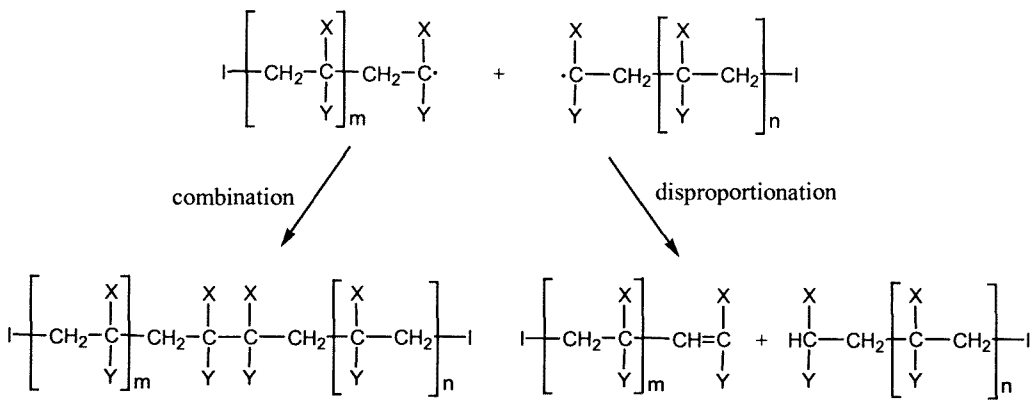
Initiation:



Propagation:

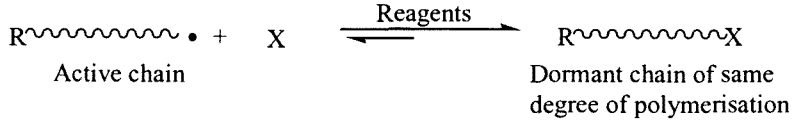


Termination:



In order to have better control over the chain architecture of the polymer, the statistical destruction of the chain propagating radicals through termination reactions must be minimised. The techniques developed for this purpose have been labelled controlled/living free radical polymerisation processes.[63] The general feature of these techniques is that the chain propagating radicals are converted into a "dormant" form which is in equilibrium with the "active" form (Scheme 2.17).

Scheme 2.17: Generalised representation of the exchange between active and dormant forms of the propagating chains in controlled free radical polymerisation.



By keeping the concentration of the "active" propagating radicals very low, under the appropriate conditions, the rate at which they terminate by self reaction is significantly reduced. If exchange between active and dormant forms is rapid, the conditions are also such that all living chains have an equal probability of growth per unit time. If these also have approximately the same total lifetime (e.g. initiated at about the same time, with very little termination), this gives rise to polymers with low polydispersity indices ($\bar{M}_w$ $/\bar{M}_n$ < 1.5). In principle, the number average molar mass of the polymer at a given conversion of monomer can be predicted because the concentration of the reagents used dictates the number of chains that are expected to be formed. This will be explained in more detail in section 2.4.4.2, using reversible addition-fragmentation chain transfer (RAFT) polymerisation as an example. Ideally, when the polymerisation reaction is stopped, the vast majority of the polymer chains are in the dormant form (with few dead chains formed by termination), i.e., they possess an end group that can be reactivated. In the presence of a second monomer, these chains can be reactivated to give rise to A-B block copolymers, again with low polydispersities. The characteristics of a living polymerisation are discussed by Quirk and Lee who give the following experimentally observable criteria.[64]

1. Polymerisation proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerisation.
2. The number average molar mass is linearly dependent on conversion.
3. The number of polymer chains is constant during polymerisation.
4. The molar mass can be controlled by the reaction stoichiometry.
5. Narrow molar mass distribution polymers are produced.

6. Block copolymers can be prepared by sequential monomer addition.

7. Chain end-functionalised polymers can be obtained quantitatively.

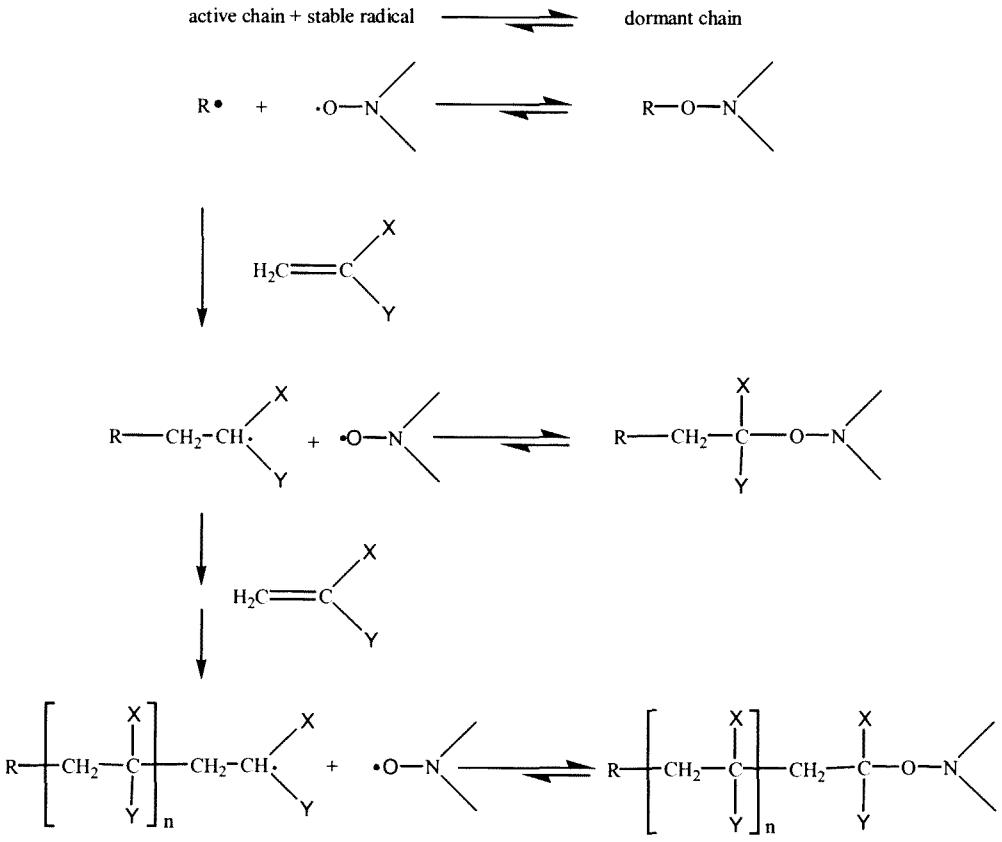
In the case of controlled radical polymerisation some of the points put forward by Quirk and Lee for traditional living polymerisation technique are not applicable. In the case of point one additional initiator is needed to continue polymerisation after full conversion was reached and additional monomer was added. Point number three states that the number of polymer chains is constant during the polymerisation, but in the case of controlled radical polymerisation there is a constant increase in the number of polymer chains.

Of late, the controlled free radical polymerisation techniques that have received the greatest attention are nitroxide-mediated polymerisation[65,66], atom transfer radical polymerisation (ATRP)[67,68] and reversible addition-fragmentation chain transfer (RAFT) polymerisation.[69,70] The first two techniques will be briefly discussed in sections 2.4.2 and 2.4.3, followed by a more detailed discussion on RAFT polymerisation in section 2.4.4, as this will be the choice of controlled free radical technique used in the experimental sections.

2.4.2 Nitroxide mediated polymerisation

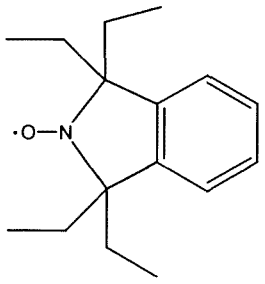
This controlled polymerisation technique was first reported by Rizzardo *et al.*[71,72] in the early 1980s. The key step in the mechanism of nitroxide-mediated polymerisation is the reversible coupling of the propagating radicals (active chains) with nitroxides to produce the corresponding alkoxyamines (dormant chains), as shown in Scheme 2.18. This provides a mechanism for the rapid deactivation of propagating radicals and an equilibrium that is strongly shifted to the dormant side. This accounts for the controlled characteristics associated with the process, such as narrow polydispersities and the ability to form block copolymers by chain extension.

Scheme 2.18: Schematic representation of the nitroxide-mediated polymerisation mechanism.



A variety of nitroxides have been used in this process to mainly polymerise styrene and styrene derivatives. Some of those nitroxides found to be most effective include (Scheme 2.19): 1,1,3,3-tetraethyl-2,3-dihydro-1*H*-isoindolin-2-yloxyl (**1**), 2,2,6,6-tetramethylpiperidin-2-oxyl (**2**) (TEMPO), di-*tert*-butyl nitroxide (**3**),[73-75] 2,2,5-trimethyl-3-(1'-phenylethoxy)-4-phenyl-3-azahexane (**4**)[76,77] and N-tert-butyl-N[1-diethyl phosphono-(2,2-dimethylpropyl) nitroxide (**5**).[78,79] The latter (4) and (5) are two examples of more versatile nitroxides that are additionally applicable to the polymerisation of other monomers, e.g. acrylates and conjugated dienes. Nitroxide-mediated polymerisation has certain disadvantages, such as use for only a limited range of monomers, other than styrene and styrene derivatives, and the required optimum reaction temperatures are usually high.

Scheme 2.19: Examples of nitroxides that have been successfully used in nitroxide–mediated polymerisation.



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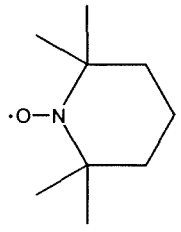

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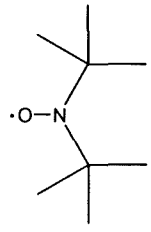

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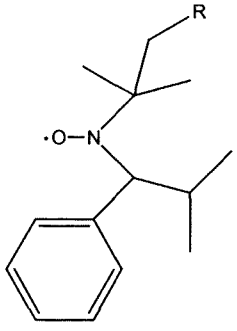

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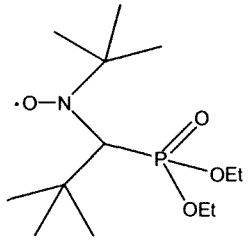

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2.4.3 Atom transfer radical polymerisation (ATRP)

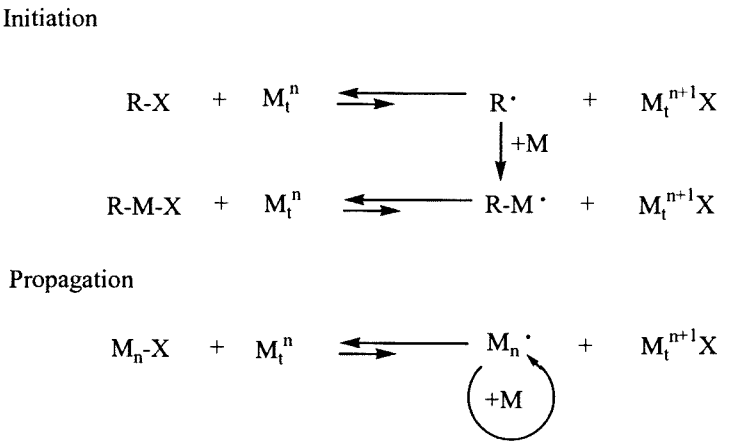
ATRP is another controlled radical polymerisation technique based on reversible deactivation of the chain propagating radicals.[67,80,81] This process makes use of a simple alkyl halide, R-X (X = Cl and Br), as an initiator and a transition metal species complexed by suitable ligand(s), M_t^n/L_x. A widely investigated system is based on copper (with transitions between Cu(II) and Cu(I)), but nickel, palladium, ruthenium and iron also have been used with suitable performance. A popular ligand used in ATRP systems is 2,2'-bipyridine. The reaction mechanism for ATRP is shown in Scheme 2.20.

Initially, the transition metal species, M_t^n, abstracts the halogen atom X from the organic halide, R-X, to form the oxidised species, $M_t^{n+1}X$, and the carbon centred radical, $R^{\bullet}$. In the following step, the radical, $R^{\bullet}$, reacts with monomer, M, to form the intermediate radical species, R-M$^{\bullet}$. The target product, R-M-X, is a result of the reaction between

$M_t^{n+1}X$ and R-M·. This regenerates the reduced transition metal species, M_t^n, which then reacts further with R-X and promotes a new redox cycle. The high efficiency of the transition metal catalysed atom transfer reaction in producing the target product, R-M-X, effectively induces a low concentration of free radicals, resulting in much less frequent termination reactions between radicals.

A major drawback restricting the industrial applications of ATRP is the removal of metal ions from the final polymer product. ATRP of acidic monomers have generally been proved to be more problematic. This is because carboxylic acid-based monomers such as methacrylic acid or acrylic acid form insoluble complexes with the copper catalyst when ATRP is attempted in nonaqueous media

Scheme 2.20: Schematic representation of the ATRP mechanism.



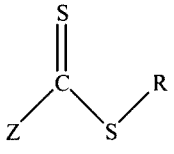
2.4.4 Reversible addition fragmentation chain transfer (RAFT) polymerisation

2.4.4.1 Introduction

A novel "living" free-radical polymerisation technique was published by Rizzardo *et al.* in 1998. Because the mechanism involved a reversible addition-fragmentation chain transfer step it was named the RAFT process.[69] The RAFT process has shown to be one of the more robust and versatile techniques by which to synthesise polymers of predetermined molar mass and narrow polydispersities (< 1.5). The first species to be used as RAFT agents were methacrylate macromonomers, but they were not very effective.[82,83] The breakthrough came with the use of a more reactive double bond

species, of general structure S=C(Z)-SR (**1**). Scheme 2.21 shows some further examples. RAFT polymerisation is carried out by the simple addition of a chosen quantity of a thiocarbonylthio compound to a conventional free radical polymerisation mixture (same monomers, initiators, solvents and temperature). The thiocarbonylthio compound acts as an efficient reversible addition-fragmentation chain transfer agent (RAFT agent) and confers controlled characteristics to the polymerisation.[69,84,85] Dithioesters,[69,86] dithiocarbamates,[70,87] xanthates[87] and trithiocarbonates[88,89] are examples of RAFT agents with different molecular structures that have been successfully used as chain transfer agents. A great advantage of the RAFT process is its compatibility with a wide range of monomers, including functional monomers.

Scheme 2.21: The general structure of a thiocarbonylthio RAFT agent (**1**). **2-9** are examples of different thiocarbonylthio compounds that have been successfully used as RAFT agents.



1

2 Z=Ph, R=$C(CH_3)_2Ph$

3 Z=Ph, R=$CH(CH_3)Ph$

4 Z=Ph, R=CH_2Ph

5 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CO_2H$

6 Z=Ph, R=$C(CH_3)_2CN$

7 Z=CH_3, R=CH_2Ph

8 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CH_2OH$

9 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CO_2Na$

2.4.4.2 Mechanism of the RAFT process

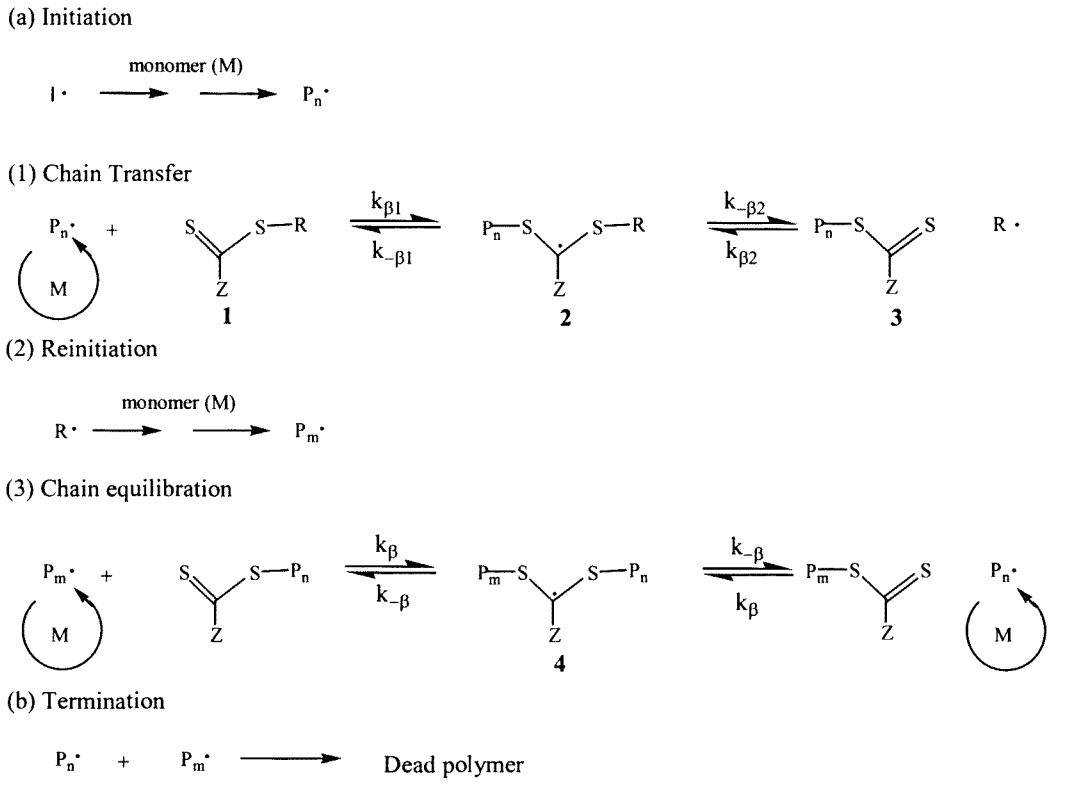
Scheme 2.22 describes the basic RAFT process. Initiator decomposition gives rise to primary radicals ($I^\bullet$), which either react with monomer units to form growing chains, leading to oligomeric propagating radicals of degree of polymerisation n ($P_n^\bullet$) after n propagation steps, or with the S=C moiety of the RAFT agent **1**. The addition of small carbon-centred radicals to the RAFT agent is in most cases rapid and not rate

determining. So the first rate-determining step involves the reaction of a propagating radical $P_n^{\bullet}$ with RAFT agent **1** to form intermediate radical **2.**

Fragmentation of the formed labile intermediate species can be either into the two original reactant species, or into a temporarily deactivated dormant polymeric RAFT agent **3** and a radical ($R^{\bullet}$) derived from RAFT agent **1**. The next step involves the re-initiation of polymerisation by the reaction of radical ($R^{\bullet}$) with monomer to form a propagating radical $P_m^{\bullet}$. The retention of the thiocarbonylthio moiety (**Z-C(S)S-**) in polymeric RAFT agent **3**, derived from the initial RAFT agent **1**, is an essential feature of the RAFT mechanism.

The subsequent addition of growing polymeric radicals to the dithiocarbonyl double bond of the dormant polymeric RAFT agent forms intermediate radical **4**, which has been directly observed by ESR spectroscopy.[90] There is approximately equal probability for the intermediate radical to fragment back into either its starting species or into a dormant polymeric RAFT agent and a polymeric radical, in which the dithiocarbonate moiety has been exchanged between the active and dormant polymer chains of the starting species. The newly formed dormant polymer chains can then be reactivated. This equal probability to fragment to both sides of the equilibrium is a result of the symmetry of the intermediate radical **4**. It is important to realise that the equilibria shown take place between the entire populations of propagating radicals and dormant chains, rather than the pair-wise reaction between a specific radical and a specific dormant chain, which might be deduced from Scheme 2.22.

Scheme 2.22: Schematic representation of the RAFT mechanism.



The end result is that most polymer chains are formed with dithiocarbonate end-groups. To enable a stepwise growth of the polymer chains, to obtain low chain length polydispersities, the rate of addition of the propagating polymeric radicals to the dithiocarbonyl double bond must be fast compared to that of propagation, so to keep the fraction of termination products low with respect to the total amount of living (capped) chains. The concentration of polymer chains at the end of the polymerisation reaction is given by equation 2.19, assuming termination by disproportionation:

$$[chains] = [RAFT] + 2\,f \cdot ([I] - [I]_0) \qquad 2.19$$

in which [RAFT] represents the concentration of dormant chains, being equal to the initial concentration of the RAFT agent , while the second term describes the number of chains that are derived from the decomposed initiator. f is an efficiency factor. The

number of chains initiated by initiator-derived radicals determines the amount of dead polymer chains formed. So, in order to obtain a high percentage of dormant chains, the initiator to RAFT agent ratio should be kept low. The theoretically expected number average molar mass as a function of time/conversion can be calculated by equations 2.20 and 2.21. FW_M is the molar mass of a monomer unit and FW_{RAFT} is the molar mass of the RAFT agent. $[M]_0$, $[I]_0$, and $[RAFT]_0$ are the initial concentrations of the monomer, initiator, and the RAFT agents, f_I is the initiator efficiency, k_d is the decomposition rate coefficient for the initiator, and x is the fractional conversion.

$$\bar{M}_{n,\,theory} = FW_{RAFT} + \frac{x\,[M]_0\,FW_M}{[RAFT]_0} \tag{2.20}$$

$$\bar{M}_{n,\,theory} = FW_{RAFT} + \frac{x\,[M]_0\,FW_M}{[RAFT]_0 + 2f_I\,[I]_0\,(1 - e^{-k_d t})} \tag{2.21}$$

Equation 2.20 neglects the contribution of initiator-derived chains to the total number of chains, and the resulting number average molar masses. Equation 2.21 includes the (time-dependent) contribution of initiator-derived chains to the total number of chains.

For the RAFT agents to show good living polymerisation characteristics there needs to be a rapid exchange of the dithiocarbonate moiety between the polymer chains. To achieve rapid exchange the rate of addition of the propagating polymeric radical to the RAFT compound must be fast with respect to addition to monomer. This means that the propagating polymeric radical must have a high reactivity towards the thiocarbonyl double bond. The activating group Z in Scheme 2.21 determines the reactivity of this bond. When, for example, a phenyl group is used as the activation group, a high rate of addition of polystyryl propagating radicals to the RAFT agent is obtained, but the same group will be less effective when vinyl acetate is polymerised. When the phenyl group is exchanged for either an oxygen or nitrogen substituent the effect is essentially reversed.[87] The effects of the Z group on a series of styrene polymerisations have been proposed by Chiefari *et al*, where the chain transfer coefficients decrease in the series where Z is Ph >

SCH_2Ph ~ SMe ~Me ~ *N*-pyrrolo >> OC_6F_5 > *N*-lactam > OC_6H_5 > O(alkyl) >> $N(alkyl)_2$. Only the first five in the series provided narrow polydispersity polystyrene ($\bar{M}_w/\bar{M}_n < 1.2$) in batch polymerisation.[91] RAFT agents with electrophilic Z constituents with lone pairs directly conjugated to the C=S double bond (O-, N<) have low transfer coefficients. However, electron-withdrawing groups on O and N (in particular, groups able to delocalise the nitrogen lone pair in the case of dithiocarbamates) can significantly enhance the activity of the RAFT agents to modify the above order. The relative effectiveness of the RAFT agents is rationalised in terms of interaction of the Z substituent with the C=S double bond to activate or deactivate that group towards free radical addition.

It is important that the RAFT agent contains a good leaving group R (Scheme 2.21), which is able to reinitiate polymerisation. From step (1) in Scheme 2.22 it can be deduced that the transfer rate coefficient, k_{tr}, is equal to:

$$k_{tr} = k_{\beta 1} \cdot \frac{k_{\beta 2}}{k_{\beta 2} + k_{-\beta 1}} \qquad 2.22$$

For all of the polymer chains to start growing at about the same time it is important that the initial transformation from RAFT agent to dormant polymer species be rapid (step 1 in Scheme 2.21). In this reaction the intermediate radical (**2**) is not symmetrical and the R group will need to be selected in such a way that it is a better leaving group than the (oligomeric) polymer chain. In step 3 all of the initial RAFT has been transformed, and the only transfer reaction is between polymeric propagating radicals and polymeric dormant species, which leads to the symmetrical intermediate radical **4**. Therefore, from step (3) it can be deduced that the transfer rate coefficient, k_{tr}, will then be equal to:

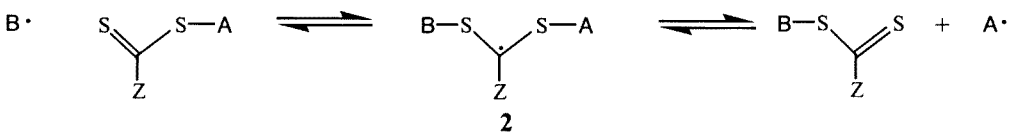
$$k_{tr} = 0.5\, k_{\beta} \qquad 2.23$$

Assuming that the rate of transfer is fast compared to that of propagation, the radical activity is exchanged rapidly among the chains. All chains then have an equal chance to add monomer and will therefore grow at the same rate.

The demands on the R group of the dithioester RAFT agents are also dependent on the monomer that is being polymerised, and the chain transfer constant decreases in the series where R is poly(methacrylyl) to poly(styryl) to poly(acrylyl).[90] Another important aspect concerning the R group is its ability to reinitiate polymerisation. Inhibition and retardation may occur if the expelled radical R has difficulty in adding to monomer. This will then result in slow conversion of the transfer agent and a broadened molar mass distribution. A number of factors (steric factors, radical stability, and polar factors) appear to be important in determining the leaving group ability of R·. The more stable, more electrophilic, and more bulky radicals are better leaving groups.[92] The leaving group ability decreases in the series where R is tertiary >> secondary > primary.[90]

The R group also plays an important role in the synthesis of block copolymers where the monomer resulting in propagating radicals with the better leaving group ability should be polymerised first.[86] The reason for this can be explained as follows: to form a narrow polydispersity AB block copolymer the first formed thiocarbonylthio compound (S=C(Z)S-A) should have a high transfer constant in the subsequent polymerisation step to give the B block. The propagating radical A•·is required to have comparable or better leaving group ability than that of the propagating radical B•·under the reaction conditions (Scheme 2.23). According to Chong et al,[84] when A is a poly(acrylate ester) or polystyrene chain, the transfer constant of S=C(Z)S-A in MMA polymerisation appears to be very slow. The reason for this is that the acrylyl- or styryl-propagating radicals are poor leaving groups in comparison to a methacrylyl-propagating radical causing the intermediate radical **2** (Scheme 2.23) to partition strongly in favour of the starting materials. This then leads to broad block copolymer products. By doing the reverse and synthesising the PMMA first, the fragmentation preferentially occurs in the direction of the right arrow, resulting in narrow block copolymer products.

Scheme 2.23: Schematic representation of the intermediate structure formed during an AB block copolymerisation.



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2.5 References

1 Larson, R. G. *The structure and Rheology of Complex Fluids*, Oxford University Press, New York, 1999, 1.

2 Abdel-Khalik, S. I.; Hassager, O.; Bird, R. B. *Polym. Eng. Sci.* 1974, 14, 859.

3 Friend, J. P.; Hunter, R. J. *J. Colloid Interface Sci.* 1971, 37, 548.

4 Uejima, H. *J Appl. Phys.* 1972, 11, 319.

5 Klingenberg, D. J.; Zukoski, C. F. *Langmuir* 1990, 6, 15.

6 Casson, N. *Rheology of Disperse Systems*, Pergamon Press, London, 1959, 84.

7 Herschel, W. H.; Bulkley, R. *Konsistenzmessungen von Gummi-Benzollosungen, Kolloid-Z* 1926, 39, 291.

8 Yamamoto, T.; Furukawa, H. *J. Appl. Polym. Sci.* 2001, 80, 1609.

9 Tiu, C.; Nicolae, G.; Tam, K. C. *J. Polym. Res.* 1996, 3, 201.

10 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 1426.

11 Glass, J. E. *Journal of Oil and Colour Chemist Association* 1975, 58, 169.

12 Glass, J. E. *Journal of Oil and Colour Chemist Association* 1976, 58, 86.

13 Patton, T. C. *Paint Flow and Pigment Dispersion*, Wiley, New York, 1979, 355.

14 Murakami, T.; Fernando, R. H.; Glass, J. E. *Journal of Oil and Colour Chemist Association* 1988, 10, 315.

15 Ma, Z.; Lundberg, D. J.; Roberts, S.; Glass, J. E. *J. Appl. Polym. Sci.* 1993, 49, 1509.

16 Sota, S. L.; Lewandowski, E. W.; Schaller, E. J. *J. Coat. Technol.* 1989, 61, 135.

17 Shay, G. D.; Olsen, K. R.; Stalings, J. L. *J. Coat. Technol.* 1996, 68, 51.

18 Just, E. K.; Majewicz, T. G. *Encyclopedia of Polymer Science and Engineering*, Wiley-Interscience, New York, 1985, 17, 226.

19 Croll, S. G.; Kleinlein, R. L. *Water Soluble Polymers: Beauty with Performance*, American Chemical Society, Washington, D.C., 1986, 333.

20 Blake, D. M. *Handbook of Coatings Additives*, Marcel Dekker, New York, 1987, 1, 43.

21 Sperry, P. R.; Hoppenberg, H. B.; Thomas, N. L. *J. Colloid Interface Sci.* 1981, 82, 62.

22 Sperry, P. R. *J. Colloid Interface Sci.* 1982, 87, 375.

23 Sperry, P. R. *J. Colloid Interface Sci.* 1984, 99, 97.

24 Gohman, R. G. *Am. Paint Coatings J.* 1983, 42.

25 Griffith, K. A. *Journal of Water Borne Coatings* 1987, 10, 2.

26 Shaw, K. G.; Leopold, D. P. *J. Coat. Technol.* 1985, 57, 63.

27 Rokowski, J. M.; Schaller, E. J.; Aviles, R. G. *Proceedings of the 14th International Congress, Organic Coatings Science & Technology,* Athens, Greece, 1988, 37.

28 Annable, T.; Ettlaie, R. *Macromolecules* 1994, 27, 5616.

29 Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*, Academic, New York, 1983, 17.

30 Char, K.; Frank, C. W.; Gast, A. P.; Tang, W. T. *Macromolecules* 1987, 20, 1833.

31 Persson, K.; Abrahamsen, S.; Stilbs, P.; Hansen, F. K.; Walderhaug, H. *Colloid. Polym. Sci* 1992, 270, 465.

32 Fonnum, G.; Bakke, J.; Hansen, F. K. *Colloid. Polym. Sci* 1993, 271, 380.

33 Annable, T.; Buscall, R.; Ettelai, R.; Whittlestone, D. *J. Rheol.* 1993, 37, 695.

34 Scwab, F. G.; Glass, J. E. *Advances in Chemistry Series 213*, Washington DC, 1986, American Chemical Society, 375.

35 Hall, J. E. *J. Coat. Technol.* 1986, 58, 65.

36 Glass, J. E.; Fernando, R. H.; England-Jongewaard, S. K.; Brown, R. G. J. *Journal of Oil and Colour Chemist Association* 1984, 67, 256.

37 Fernando, R. H.; Glass, J. E. *Journal of Oil and Colour Chemist Association* 1984, 67, 279.

38 Glancy, C. W.; Basset, D. R. *Proc ACS Div Polym Mater Sci Eng* 1984, 51, 348.

39 Vebrugge, G. D. *J. Appl. Polym. Sci.* 1970, 14, 897.

40 Shay, G. *Surface Coatings International* 1993, 11, 446.

41 Muroi, S. *J. Appl. Polym. Sci.* 1966, 10, 713.

42 Muroi, S.; Hosoi, K.; Ishikawa, T. *J. Appl. Polym. Sci.* 1967, 11, 1963.

43 Loncar, F. V.; El-Aasser, M. S.; Vanderhoff, J. W. *Polym. Mater. Sci. Eng* 1985, 52, 299.

44 Sprong, E.; de Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *J. Polym. Sci., Part A: Polym. Chem.* 2003, 41, 223.

45 Verbrugge, C. J. *J. Appl. Polym. Sci.* 1970, 14, 911.

46 Yudelson, J. S.; Mack, R. E. *J. Polym. Sci., Part A: Polym. Chem.* 1964, 2, 4683.

47 Sokota, K.; Okaya, T. J. *J. Appl. Polym. Sci.* 1976, 20, 2583.

48 Thiebeault, J. C.; Sperry, P. R.; Schaller, E. J. *J. Proc. ACS Div. Polym. Mater. Sci. Eng.* 1984, 51, 353.

49 Sperry, P. R.; Thiebeault, J. C.; Kostansek, E. C. *Proceedings of the 11th International Conference on Organic Coatings Science and Technology,* 1985, 1.

50 Schaller, E. J. *Journal of Surface Coatings Australia* 1985, 22, 6.

51 English, R. J.; Raghavan, S. R.; Jenkins, R. D.; Kjan, S. A. *J. Rheol.* 1999, 43, 1175.

52 Thiebeault, J. C.; Sperry, P. R.; Schaller, E. J. *Proc ACS Div Polym Mater Sci Eng* 1984, 51, 353.

53 Tanford, C. *In the Hydropbic Effect*, Wiley, New York, 1980, 54.

54 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 3271.

55 Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* 2000, 33, 1727.

56 Shay, G. D.; Rich, A. F. *J. Coat. Technol.* 1986, 58, 43.

57 Aubrey, T.; Moan, M. *J. Rheol.* 1996, 40, 441.

58 Tam, K. C.; Seng, W. P.; Jenkins, R. D.; Bassett, D. R. *J. Polym. Sci., Part B: Polym. Phys.* 2000, 38, 2019.

59 Pham, Q. T.; Russel, W. B.; Lau, W. *J. Rheol.* 1998, 42, 159.

60 Moad, G.; Soloman, D. H. *The Chemistry of Free Radical Polymerization*, Elsevier Science Ltd, 1995, 1.

61 Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*, Academic Press, London, 1995, 14.

62 Benson, S. W.; North, A. M. *Journal of American Chemical Society* 1962, 84, 935.

63 Matyjaszewski, K. *ACS Symp. Ser.* 1998, 685, 2.

64 Quirk, R. P.; Lee, B. *Polym. Inter.* 1992, 27, 359.

65 Chong, B. Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. *Macromolecules* 1999, 32, 6895.

66 Okamura, H.; Takatori, Y.; Tsunooka, M.; Shirai, M. *Polymer* 2002, 43, 3155.

67 Wang, J.-S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.

68 Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* 2000, 33, 255.

69 Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.

70 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.

71 Solomon, D. H.; Rizzardo, E.; Cacioli, P. *U.S. Patent 4581429* 1985, (Chemical Abstr. 1985, 102:221335q).

72 Rizzardo, E. *Chemistry in Australia* 1987, 54, 32.

73. Solomon, D. H.; Rizzardo, E.; Cacioli, P. *U. S. Patent 4581429*, 1985.

74 Colombani, D. *Prog. Polym. Sci.* 1997, 22, 1649.

75 Otsu, T.; Matsumoto, A. *Adv. Polym. Sci.* 1998, 136, 75.

76 Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* 2000, 33, 363.

77 Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russel, T. P. *Macromolecules* 2000, 33, 1505.

78 Grimaldi, S.; Finet, J.-P.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Gnanou, Y.; Fontanille, M.; Nicol, P.; Pierson, J.-F. *ACS, Polym. Prepr.* 1997, 38, 651.

79 Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* 2000, 122, 5929.

80 Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.

81 Matyjaszewski, K.; Pattern, T. E.; Xia, J. *J. Am. Chem. Soc.* 1997, 119, 674.

82 Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* 1995, 28, 5381.

83 Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* 1996, 111, 13.

84 Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.

85 Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* 2000, 150, 33.

86. Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. WO 98/01478*, 1998.

87. Chiefari, J.; Mayadunne, R. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. WO 9931144*, 1999.

88 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* 2000, 33, 243.

89 Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* 2002, 35, 6754.

90 Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 5457-5459.

91 Chiefari, J.; Mayadunne, R. T.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* 2003, 36, 2273.

92 Chong, B. Y. K.; Krstina, J.; Le, T. P.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* 2003, 36, 2256.

CHAPTER 3

Synthesis, Characterisation and Rheological Properties of Model Alkali-Soluble Rheology Modifiers Using the *In Situ* Formation of 2-Cyanoprop-2-yl Dithiobenzoate as the RAFT Agent

Synopsis: *Model alkali-soluble rheology modifiers of different molar masses were synthesised by the RAFT polymerisation of methyl methacrylate, methacrylic acid and two different hydrophobic macromonomers.*

The polymerisation kinetics showed good living character including well-controlled molar mass, molar mass linearly increasing with conversion and the ability to chain extend by forming an AB block copolymer.

The steady-shear and dynamic properties of a core-shell emulsion, thickened with the different model alkali-soluble rheology modifiers, were measured. The core-shell emulsion showed contrasting rheological behaviour when thickened with the conventional or associative rheology modifiers, respectively.

3.1 Introduction

As has been discussed in chapter 2, alkali-soluble polymers, especially hydrophobically modified polymers, are extensively used as thickeners and rheology modifiers in a variety of industrial products. The concentration, molar mass and chain architecture of the polymers are important factors that influence the thickening behaviour of the rheology modifiers.[1-4] A wide variety of ethylenically unsaturated monomers and a wide range of synthetic techniques, including precipitation polymerisation in organic diluents, solution polymerisation in organic solvents, and aqueous emulsion polymerisation have been used to prepare these polymers.[5] This chapter will focus on the solution polymerisation in organic solvent of the alkali-soluble rheology modifiers

To overcome the process limitations (poor control over the molar mass distribution, end group functionalities, and chain architecture of the polymers) of conventional free radical polymerisation, the RAFT process will be used as controlled free radical polymerisation technique.[6-9] This technique allows the synthesis of polymers of controlled molar mass, narrow polydispersity and tailored chain architecture.

The synthesis of model compounds allows the possibility of investigating the relationship between the rheological properties of the alkali-soluble rheology modifiers and their specific molar mass and chain architecture.

3.2 Experimental

3.2.1 Reagents

Methyl methacrylate (MMA, 98%) and methacrylic acid (MAA, 98%) were obtained from the Plascon Research Centre, University of Stellenbosch. The MMA was washed with a 0.3 M solution of KOH and distilled under vacuum to remove the inhibitor. The nonylphenyl surfactants, containing on average 100 (HM 4, 99%) and 5 (HM 1, 99%) oxyethylene groups, were purchased from Sigma-Aldrich and used as received. 2,2-Azobis(isobutyronitrile) (AIBN, Delta Scientific, 98%) was recrystallised twice from methanol.

The following chemicals were used in the synthesis of the macromonomers and the RAFT agent: acryloyl chloride (Acros, 99%), bromobenzene (Fluka, 99%), carbon disulfide (Sigma-Aldrich, 99.9%), 33% HCl solution (Sigma-Aldrich), dimethyl sulfoxide (DMSO, Saarchem, 99.5%), and iodine crystals (Fluka). These reagents were all used as received.

THF (Sigma Aldrich, 99%) were dried before use. Magnesium turnings (Unilab) were used as received. All water used was first distilled, and passed through a Milli-Q (Millipore) ion exchange filtration system (DDI water).

3.2.2 Analyses

Size exclusion chromatography (SEC): The molar masses and molar mass distributions of the polymers were measured by size exclusion chromatography. The chromatograph used was a Waters 600E module with a Waters 410 differential refractometer. THF was used as mobile phase with a flow rate of 1.0 mL min^{-1} at a column temperature of 35 °C. Four Phenogel columns (300 mm × 7.80 mm) with respective pore sizes of 100, 10^3, 10^4 and 10^5 Å were used in series. The system was calibrated using nine narrow molar mass PMMA standards, in the range of 2500 – 900 000 g mol^{-1}, supplied by Pressure Chemicals. Molar masses are reported as PMMA equivalents. Prior to SEC analysis, methacrylic acid groups were converted to methyl methacrylate units with tetramethylammonium hydroxide and methyl iodide in THF at 80 °C.[9]

^{1}H NMR: All ^{1}H NMR spectra of the bis(thiocarbonyl) disulfide RAFT agent, unreacted surfactants and the associative macromonomers were obtained using a Varian VXR 300 spectrometer operating at 300 MHz. All spectra obtained were calibrated using 0.05% TMS as the internal standard.

^{13}C NMR: The polymers from reactions 7 and 8 were analysed by ^{13}C NMR spectroscopy, using a Varian VXR 300 spectrometer operating at 75 MHz. All spectra obtained were calibrated using 0.05 % TMS as the internal standard.

FTIR: FTIR spectra were recorded as films on sodium chloride discs on a Paragon 1000 FTIR spectrometer.

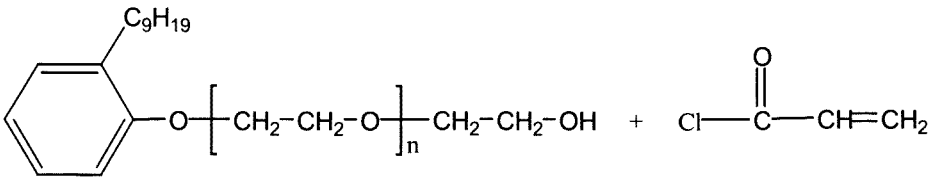
Rheology: The rheological analyses of the various samples were performed on a Haake Rheostress RS 150 rheometer. All samples were tested in controlled rate (CR) and controlled stress (CS) measuring modes, using a 1° cone and plate measuring system.

Sample preparation and analysis: All synthesised polymer samples were precipitated using a 2.5 % (m/v) solution of hydroquinone in methanol. **SEC:** Samples were prepared for SEC analysis by drying the polymer *in vacuo* and redissolving *ca.* 5 mg of the polymer in 1 mL THF. **^{1}H–NMR:** The RAFT agent, surfactant and macromonomer samples for the NMR analysis were prepared by dissolving 65 mg of the sample in 0.65 mL of deuterated chloroform ($CDCl_3$) as solvent. **^{13}C-NMR:** The RAFT agent samples were prepared by dissolving 65 mg of the sample in 0.65 mL of deuterated chloroform ($CDCl_3$) as solvent. The polymer samples of rheology modifiers 7 and 8 were prepared for NMR analysis by dissolving 65 mg of polymer in 0.65 mL of deuterated dimethyl sulfoxide (DMSO). **FTIR:** Samples for FTIR analysis were prepared by heating the surfactants and macromonomers sufficiently to lower the viscosity and enable the casting of thin films onto sodium chloride disks. **Viscosity profiles:** The rheological behaviour of the polymers was tested in a well-characterised core-shell emulsion with 46 wt% solids, an average particle diameter of 90 nm, pH 8.7 and T_g (DSC) of –5 °C. The core-shell polymer consisted of the following monomers and ratios. Core: methyl methacrylate (MMA, 80 wt %), butyl acrylate (BA, 17 wt %) and methacrylic acid (MAA, 3 wt %). Shell: butyl acrylate (BA, 63 wt %), methyl methacrylate (MMA, 31 wt %) and methacrylic acid (MAA, 3 wt %). The emulsion had a core:shell mass ratio of 5:2. The emulsion was diluted 50 % by the addition of DDI water, and 3 wt % alkali-soluble thickener with respect to the undiluted emulsion was added.

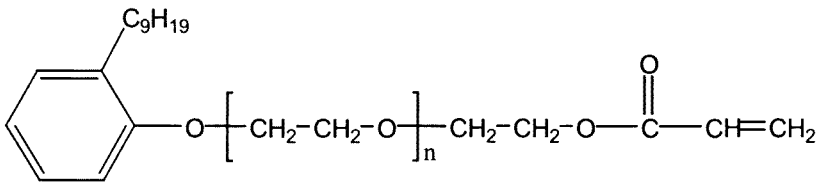
3.2.3 Synthesis of hydrophobic macromonomers

Nonylphenol surfactant (0.0111 mol, HM1 = 4.84 g or HM4 = 51.68 g) was dissolved in 250 mL of tetrahydrofuran. Acryloyl chloride (10 g, 0.11 mol) was added drop wise over a period of one hour at 0 °C. Once the reaction was completed the reaction solvent and excess acryloyl chloride were removed by evaporation under vacuum (HM1 = 4.75 g, 99% yield and HM4 = 51.15 g, 98% yield). The reaction schematic is shown in Scheme 3.1.

Scheme 3.1: The reaction schematic for the synthesis of the hydrophobic macromonomers from the reaction of acryloyl chloride with a nonionic surfactant (HM1: n = 5; HM4: n = 100).



Nonionic surfactant Acryloyl chloride



Hydrophobic macromonomer

The product was identified by **^{1}H-NMR** (HM: 30 °C, $CHCl_3$): δ 7.19 (m, 2H, aromatic), 6.83 (m, 2H, aromatic), 6.43 (ethylenic, *cis* to ester, "A" part of an ABC system, 1H, J_{AB}=1.53 Hz, J_{AC}=17.4 Hz), 6.16 (ethylenic, *gem* to ester, "C" part of an ABC system, 1H, J_{BC}=10.37 Hz), 5.84 (ethylenic, *trans* to ester, "B" part of an ABC system, 1H), 4.11 (t, 2H, $ArOC\underline{H}_2$), 3.85 (t, 2H, $ArOCH_2C\underline{H}_2$), 3.72 (m, 76H, $-(O-C\underline{H}_2C\underline{H}_2)_n-$), 4.32 (t, 2H, $C\underline{H}_2OCO$) (for this last peak, no corresponding residual peak at 3.61 ppm for unreacted surfactant was observed, *i.e.* complete conversion had occurred). **FTIR (cm^{-1}):** 1725 (carbonyl), 1633 (carbon-carbon double bond); the broad OH resonance at 3480 cm^{-1} from the unreacted surfactant is absent in the product, confirming that the esterification reaction had proceeded to virtually 100% conversion. Both of the observed spectra were consistent with the structure of the expected macromonomers. The ^{1}H-NMR

and FTIR spectra of the surfactants and associative macromonomers are shown in Figures A.1-A.4 in Appendix A.

3.2.4 Synthesis and characterisation of bis(thiocarbonyl) disulfide (RAFT-coupled product)

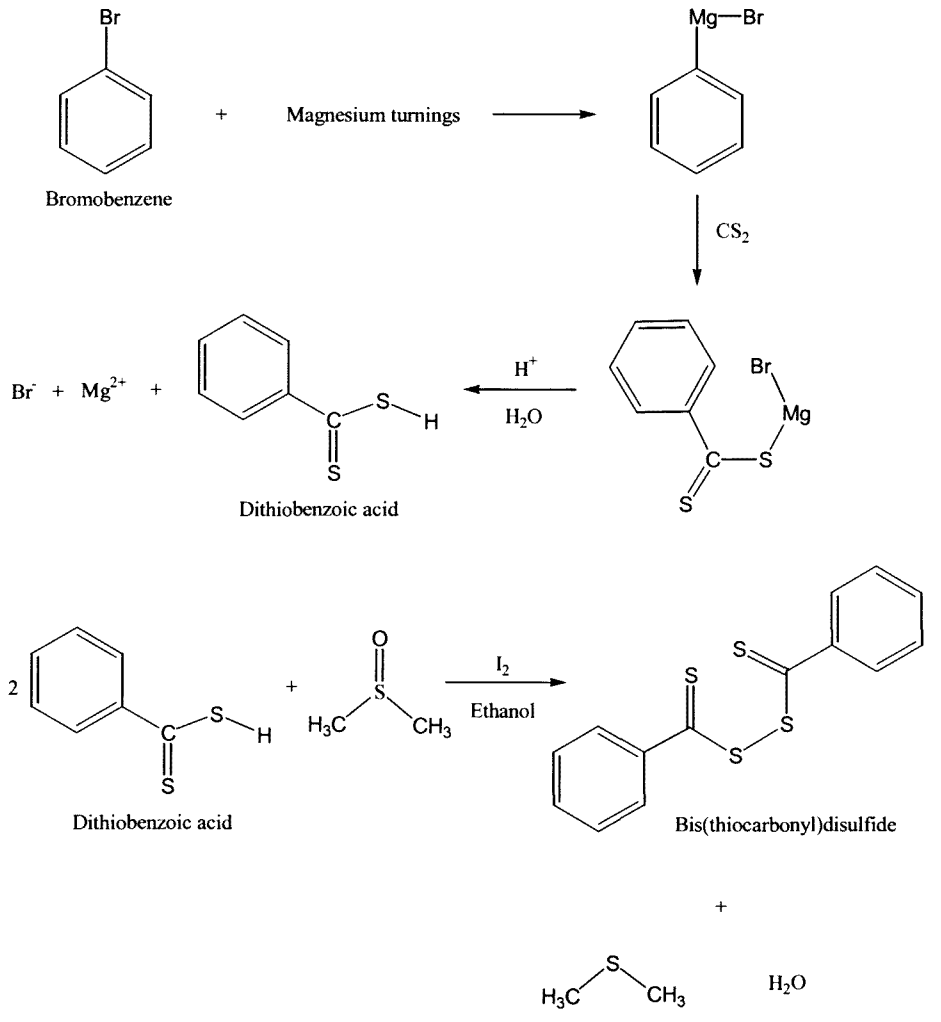
The synthesis was based on the reaction of Rizzardo et al.[10] The reaction schematic is given in Scheme 3.2.

Magnesium turnings (3.00 g) were placed in a reaction vessel with a catalytic amount of iodine. Bromobenzene (1.88 g, 0.0120 mol) and dry THF (10 mL), corresponding to 10 % of the total amounts used of these reagents, were added to the reactor, and heated slightly. The remaining THF (80 mL) and bromobenzene (16.96 g, 0.108 mol) were slowly added with cooling, such that the temperature was kept below 40 °C. Carbon disulfide (9.15 g, 0.12 mol) was added drop wise to the Grignard mixture with cooling. The Grignard reagent was then hydrolysed by the slow addition of water. The magnesium salts were removed by filtration, and washed with water.

Fuming HCl was used to acidify the reaction mixture to form the thioacid. The colour of the reaction mixture changed to a pink/purple. The formed dithiobenzoic acid was extracted with diethyl ether, to yield a product with a deep red colour. The THF and diethyl ether were removed by evaporation under vacuum.

A catalytic amount of iodine and DMSO (18.75 g, 0.240 mol) were added to the acid in absolute ethanol. The reaction proceeded at room temperature and the product bis(thiocarbonyl) disulfide (15.61 g, 85 % yield) precipitated as red/purple coloured crystals. The product was filtered and dried under vacuum. It was characterised by the following signals in the ^{1}H NMR spectrum, δ (ppm): 7.49 (m, 4H, meta position), 7.65 (m, 2H, para position), 8.12 (d, 4H, ortho position). The ^{1}H NMR spectrum of bis(thiocarbonyl) disulfide is shown in Figure A.5 in Appendix A .

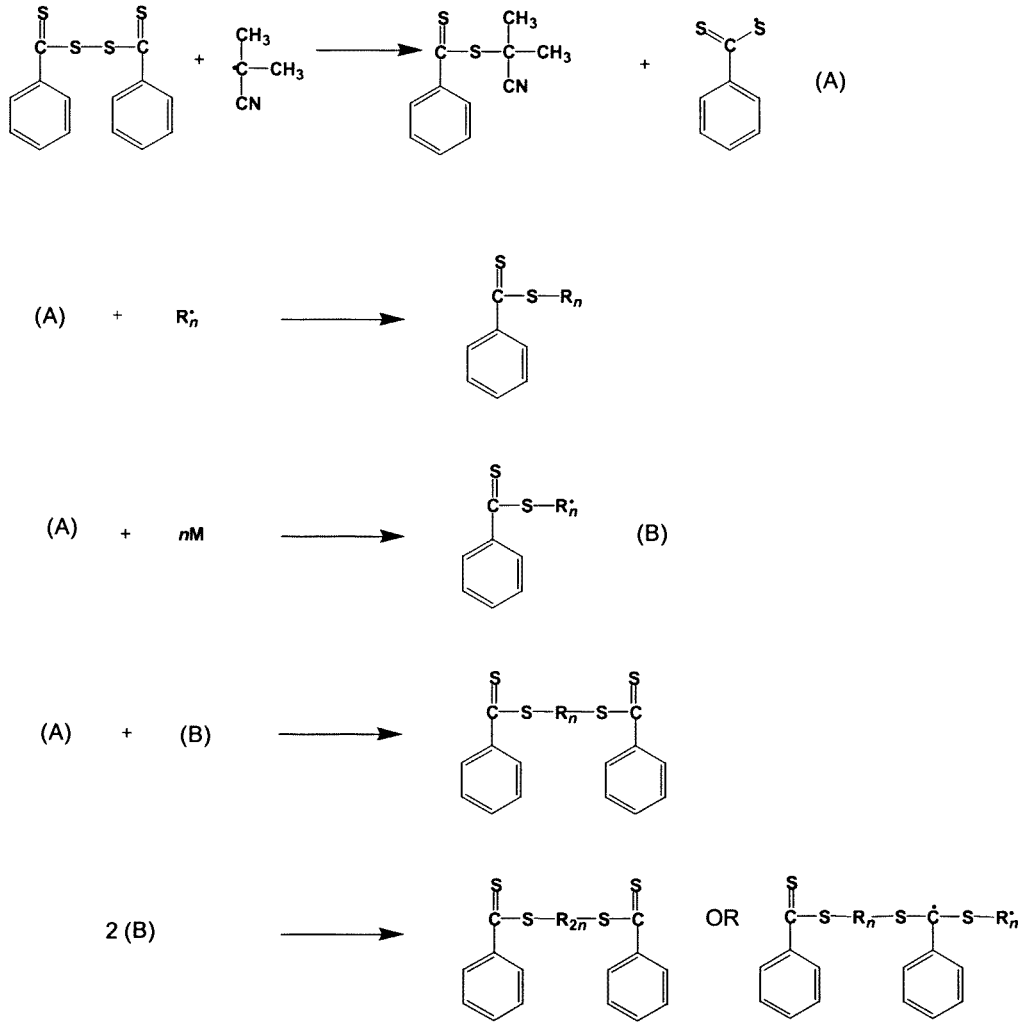
Scheme 3.2: The reaction schematic for the synthesis of bis(thiocarbonyl) disulphide.



3.2.5 In situ formation of 2-cyanoprop-2-yl dithiobenzoate

All polymers described in this chapter were synthesised by the *in situ* formation of the RAFT chains by the reaction of AIBN with bis(thiocarbonyl) disulfide. The production of the growing RAFT chains and possible side reactions via the *in situ* generation process are shown in Scheme 3.3.[11]

Scheme 3.3: Reactions that may occur from the reaction of bis(thiocarbonyl) disulfide with AIBN initiator.



3.2.6 Synthesis of conventional alkali-soluble rheology modifiers

The conventional alkali-soluble thickeners were synthesised by the copolymerisation of methyl methacrylate and methacrylic acid in the presence of the coupled RAFT agent bis(thiocarbonyl) disulfide (which released uncoupled RAFT agent via reaction with AIBN during the reaction). Three copolymers with different molar masses were

synthesised. The quantities of the different reagents used in the three reactions are shown in Table 3.1.

The general procedure for the three reactions was as follows: a reactor was charged with 1,4-dioxane (80 mL, solvent) and the monomers added. UHP grade nitrogen gas was bubbled through the reaction mixture for 30 min to remove oxygen. The initiator (AIBN) and the chain transfer agent were separately dissolved in the solvent (10 mL) and added to the reactor. The reactor was heated to 80 °C for 5 hours. Samples were drawn periodically to follow the growth of the polymer chains. After the reaction was complete, the polymer solution was left to cool to room temperature. The polymer was then precipitated with *n*-pentane and dried under vacuum. The dried polymer was pink in colour with no noticeable odour.

Table 3.1: Quantities of reagents used in the synthesis of the conventional alkali-soluble thickeners by the *in situ* RAFT solution reaction (1,4-dioxane, 100mL) of AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate (10 g, 0.100 mol) and methacrylic acid (10 g, 0.116mol) at 80 °C.

Reagent	Reaction 1	Reaction 2	Reaction 3
Bis(thiocarbonyl)disulfide	0.1556 g 0.00051 mol	0.0519 g 0.00017 mol	0.0311 g 0.000102 mol
AIBN	0.1256 g 0.00077 mol	0.0418 g 0.000255 mol	0.0251 g 0.000154 mol

3.2.7 Synthesis of alkali-soluble rheology modifiers containing hydrophobic macromonomers

Alakli-soluble polymers containing the hydrophobic macromonomers were synthesised by two methods – copolymerisation of the MMA/MAA backbone monomers with the hydrophobic macromonomers and the addition of the hydrophobic macromonomers as a second block to the living first block that consisted of RAFT-capped p(MMA-*co*-MAA).

3.2.7.1 Copolymerisation with the hydrophobic macromonomer

Rheology modifiers with three different molar masses were synthesised by the method described above; these three polymers also contained the hydrophobic macromonomer containing 100 ethylene oxide groups (HM4). Table 3.2 shows the reagents and quantities used in reactions 4 – 6 and 9. Reaction 9 contained the shorter hydrophobic macromonomer (HM1), with only 5 ethylene oxide spacer units. The dried polymer was light orange in colour with no noticeable odour.

Table 3.2: Quantities of reagents used in the synthesis of the associative rheology modifiers by the *in situ* RAFT solution reaction (1,4-dioxane, 100mL) of AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate (10g, 0.100 mol), methacrylic acid (10 g, 0.116 mol) and hydrophobic macromonomers at 80 °C.

Reagent	Reaction 4	Reaction 5	Reaction 6	Reaction 9
Hydrophobic macromonomer	(HM 4) 9.35 g 0.002 mol	(HM 4) 9.35 g 0.002 mol	(HM 4) 9.35 g 0.002 mol	(HM 1) 0.57 g 0.0025 mol
Bis(thiocarbonyl) disulfide	0.1556 g 0.00051 mol	0.0519 g 0.00017 mol	0.0311 g 0.000102 mol	0.0156 g 0.000051 mol
AIBN	0.1256 g 0.00077 mol	0.0418 g 0.000255 mol	0.0251 g 0.000154 mol	0.0126 g 0.000077 mol

3.2.7.2 Addition of the hydrophobic macromonomer as a second block

In reaction 7, a random copolymer was synthesised from MMA and MAA by the procedure described in Section 3.2.7.1. After the reaction, the polymer was precipitated in *n*-pentane and dried under vacuum to ensure that all unreacted monomer was removed. The polymer (rheology modifier 7) was then redissolved in 1,4-dioxane. The longer hydrophobic macromonomer (HM4) and AIBN were then added to the reaction vessel

and the reaction was carried out at 80 °C. Table 3.3 lists the reagents and quantities used in synthesising rheology modifier 7 and 8.

Table 3.3: Quantities of reagents used in the synthesis of the AB block copolymers by the *in situ* RAFT solution reaction of AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate, methacrylic acid and hydrophobic macromonomer HM 4 at 80 °C.

Reagent	**Reaction 7**	**Reaction 8**
1,4-Dioxane	100 mL	100 mL
Methyl methacrylate	14.00 g 0.1398 mol	
Methacrylic acid	6.00 g 0.0697 mol	
Bis(thiocarbonyl) disulfide	0.0156 g 0.000051 mol	
AIBN	0.0126 g 0.000077 mol	0.0126 g 0.000077 mol
Polymer from reaction 7		12.00 g
Macromonomer (HM4)		3.00 g 0.000652 mol

3.3 Results and discussion

3.3.1 Polymerisation reactions

The molar masses, polydispersities, and monomer ratios of polymers formed in reactions 1 – 9 (referred to as rheology modifiers 1 – 9, respectively) are shown in Table 3.4.

Table 3.4: The monomer ratios and SEC results for the polymerisation of the different rheology modifiers by the *in situ* RAFT solution (1,4-dioxane) reaction of AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate, methacrylic acid and hydrophobic macromonomers at 80 °C.

Reaction	Composition	Monomer ratio	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	MMA/MAA (random copolymer)	50/50	18500	24800	1.34
2	MMA/MAA (random copolymer)	50/50	45400	70400	1.55
3	MMA/MAA (random copolymer)	50/50	67600	105000	1.56
4	MMA/MAA/HM4 (random copolymer)	49.5/49.5/1	18500	28490	1.54
5	MMA/MAA/HM4 (random copolymer)	49.5/49.5/1	26600	41762	1.57
6	MMA/MAA/HM4 (random copolymer)	49.5/49.5/1	40700	63900	1.57
7	[MMA/MAA] [block A]	[70/30] [block A]	66800	91400	1.37
8	[MMA/MAA][HM4] [block A][block B]	[70/30][2 units] [block A][block B]	76100	99400	1.31
9	MMA/MAA/HM1 (random copolymer)	49.5/49.5/1	78300	122000	1.56

The living characteristics of the RAFT polymerisation reactions are underlined by the good linear relationship between the number average molar mass and conversion displayed in Figure 3.1 (reaction 1).[12]

The calculated number average molar mass ($\bar{M}_{n,\,theory}$) is represented by the solid and dashed curves in Figure 3.1, calculated by equations 3.1 and 3.2. FW_M is the molar mass of a monomer unit and FW_{RAFT} is the molar mass of the RAFT agent. $[M]_0$, $[I]_0$, and $[RAFT]_0$ are the initial concentrations of the monomer, initiator, and the RAFT agents, f_I is the initiator efficiency, k_d is the decomposition rate coefficient for the initiator, and x is the fractional conversion.

$$\bar{M}_{n,\,theory} = FW_{RAFT} + \frac{x\,[M]_0\,FW_M}{[RAFT]_0} \qquad 3.1$$

$$\bar{M}_{n,\,theory} = FW_{RAFT} + \frac{x\,[M]_0\,FW_M}{[RAFT]_0 + 2f_i\,[I]_0\,(1 - e^{-k_d t})} \qquad 3.2$$

Equation 3.1 neglects the contribution of initiator-derived chains to the total number of chains, and the resulting average molar masses. Equation 3.2 includes the (time-dependent) contribution of initiator-derived chains to the total number of chains. Neither equation accounts for products from non-reversible radical-radical termination.

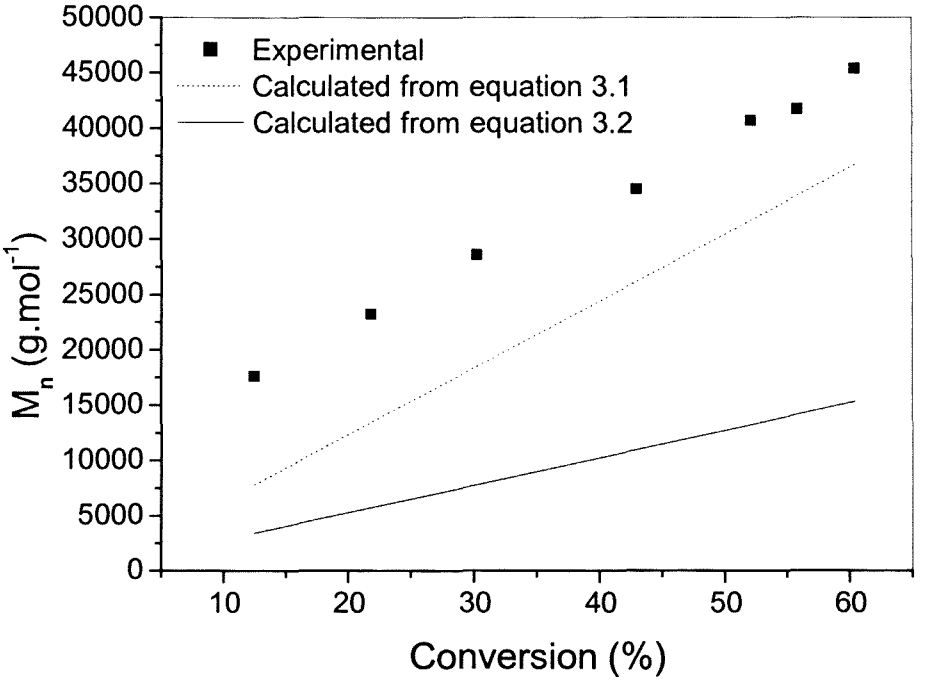


Figure 3.1: The calculated and experimental number average molar mass versus conversion for polymerisation reaction 2 by the *in situ* RAFT solution (1,4-dioxane) reaction of AIBN (0.255 mmol), bis(thiocarbonyl) disulfide (0.17 mmol), methyl methacrylate (0.100 mol) and methacrylic acid (0.116 mol) at 80 °C.

Equations 3.1 and 3.2 assume the rapid and complete conversion of the starting coupled RAFT agent into usable RAFT species. In the case of the *in situ* formation of the RAFT agent these equations do not hold for a number of reasons. The first is that the amount of available RAFT agent changes with time as the coupled RAFT agent forms usable RAFT

species (this is strongly correlated to the rate of initiator decomposition). Secondly, it is possible that there could be more than one RAFT agent per chain (Scheme 3.3). Thirdly, the possibility of incomplete conversion of the bis(thiocarbonyl) disulfide to 2-cyanoprop-2-yl dithiobenzoate may mean that less RAFT is available to the reaction. A lower RAFT concentration at any time in the reaction will lead to longer chains than would otherwise be predicted at that time. This is consistent with the observation that, early in the reaction (when much of the RAFT agent is unavailable), the molar mass is much higher than predicted by either equation, but good subsequent control is observed. Equation 3.2 should, in principle, give better agreement with experimental results than equation 3.1, although the results suggest otherwise. Both systems almost certainly have less RAFT agent available than initially added, due to both loss processes, and the possible presence of multiple RAFT agents per chain. Combination processes are also expected in this system, leading to higher molar masses than predicted by either equation. The effects of multiple RAFT agents per chain as a result of the *in situ* RAFT formation would also increase the average molar mass (and broaden the distribution), and are discussed in more detail by Vosloo *et al.*[11] Thus, the better agreement of equation 1 with the experimental results may be fortuitous.

Figure 3.2 shows the evolution of the molar mass distributions, as observed by SEC, with conversion, for the polymer synthesised in reaction 2. Similar results were obtained for reactions 1 – 7 and 9. The distributions were relatively narrow, with little tailing to low molar mass with increasing conversion, consistent with good molar mass control and living character.

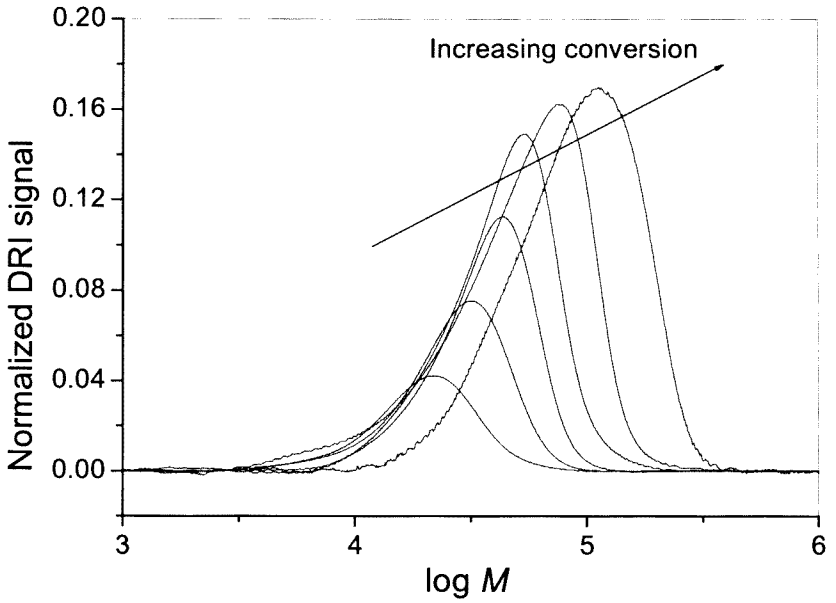


Figure 3.2: The evolution of molar mass distributions with conversion for polymerisation reaction 2 by the *in situ* RAFT solution (1,4-dioxane) reaction of AIBN (0.255 mmol), bis(thiocarbonyl) disulfide (0.17 mmol), methyl methacrylate (0.100 mol) and methacrylic acid (0.116 mol) at 80 °C.

In reaction 8 a second hydrophobic macromonomer-containing block was successfully grown onto block A (reaction 7). Once the polymerisation of the first block was stopped, the polymer chains possess a dithiobenzoate end group (remains dormant until re-activation through an encounter with a radical species) that was in the dormant state and could be reactivated. The ability to chain extend by reactivating these chains in the presence of a second monomer demonstrates the living character of the polymerisation.[8,9] The SEC traces for the block formation are shown in Figure 3.3. From the SEC data it is estimated that, on average, about two macromonomer units were added to each of the chains synthesised via reaction 7.

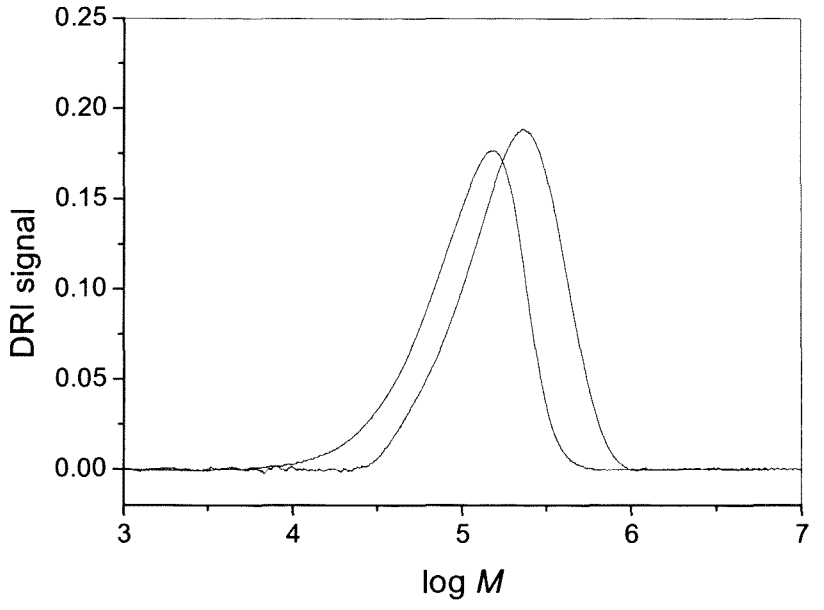


Figure 3.3: SEC traces for poly(methyl methacrylate-*co*-methacrylic acid) and poly[(methyl methacrylate-*co*-methacrylic acid)-block-(macromonomer HM 4)]. For details on molar mass refer to Table 3.4.

The macromonomers are soluble in ethanol, but the AB block copolymer is not. The block copolymer was washed repeatedly with ethanol to ensure that the macromonomers were indeed attached to the polymer chains as a second block and that it was not a blend of macromonomer and polymer (rheology modifier 7, block A). In the ^{13}C-NMR spectra of both rheology modifier 7 and 8 a septuplet (marked a in Figure A.6 and A.7 of Appendix A) is present at 39.43 ppm, which is due to the solvent (deuterated DMSO) and serves as reference peak. The ^{13}C-NMR spectrum of rheology modifier 8 (AB Block) shows a very distinctive peak (marked b in Figure A.7 of Appendix A) at 70.03 ppm that is not present in the spectrum of rheology modifier 7 (block A) and corresponds to the carbon atoms of the ethylene oxide spacer units in the macromonomers (block B).

3.3.2 Steady shear viscosity

3.3.2.1 Conventional rheology modifiers

The chemical structure of the conventional rheology modifiers consists of a random copolymer of MMA and MAA. In these polymers that contain no strongly hydrophobic regions (macromonomers), there is no strong hydrophobe-hydrophobe association.

Figure 3.4 shows the steady shear viscosity of latex solutions thickened with three conventional rheology modifiers (polymers 1 – 3) of different molar masses. All three rheology profiles show a critical stress (yield stress) at which there is a significant decrease in the viscosity of the latex solutions. An increase in the molar mass of the rheology modifiers leads to an increase in viscosity, but also gives a higher yield stress. This is typical behaviour of conventional aqueous rheology modifiers that only thicken the aqueous phase by hydrodynamic volume and molecular chain entanglement.[13] The hydrodynamic thickening mechanism of conventional alkali-soluble rheology modifiers is described in Section 2.3.5.2.[14,15]

To describe these observations in terms of a simple conceptual model: the conventional rheology modifiers can be considered analogous to a simple system of connected springs in which each polymer molecule can be thought of as a member of the ensemble of connected springs. The spring constant may be related to the molar mass of the polymer molecules. As for any system of connected springs, there is finite stress (the yield stress) at which irrecoverable failure occurs.

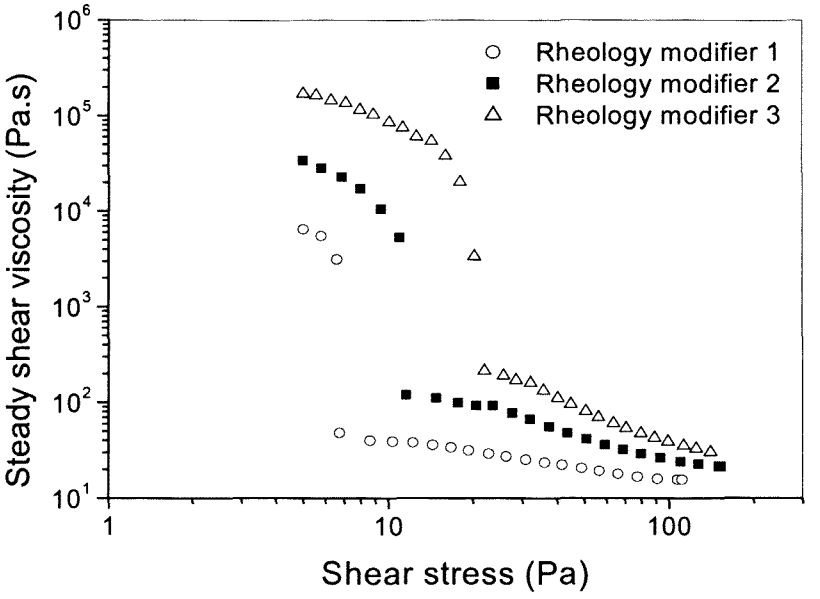
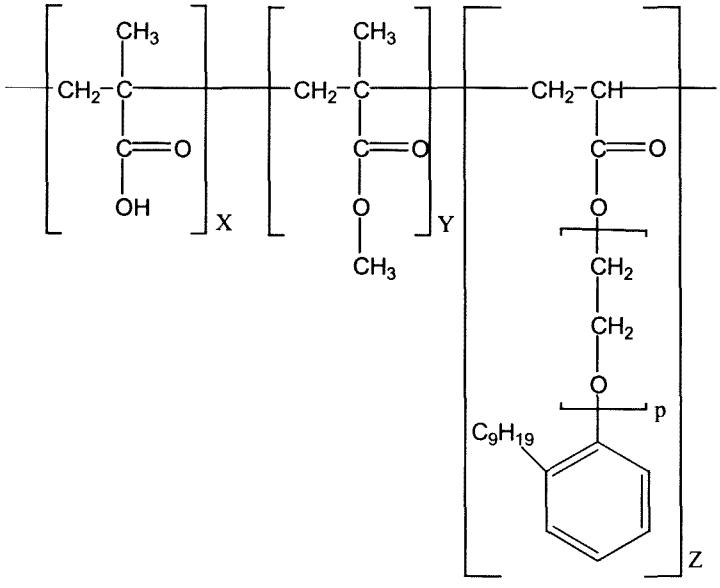


Figure 3.4: Steady shear viscosity of latex solutions thickened with conventional rheology modifiers 1 - 3.

3.3.2.2 Associative rheology modifiers

Scheme 3.4 shows the chemical structure of the associative rheology modifiers containing the hydrophobic macromonomers. The steady shear viscosity of the latex solutions thickened with associative rheology modifiers synthesised in reactions 4 – 6 is shown in Figure 3.5. All three latex solutions show shear thinning characteristics. There is a low shear viscosity plateau present which is probably the result of the hydrophobic junctions (latex-hydrophobe and hydrophobe-hydrophobe) that build the network structure, which are constantly forming, breaking and reforming by Brownian motion. This process is only present at low shear stress values for associative rheology modifiers. There is no low shear plateau present for the conventional rheology modifiers (Figure 3.4). In the higher shear stress region the occurrence of shear thinning behaviour suggests that the association network is gradually disrupted under shear. An increase in the molar mass of the rheology modifiers leads to a viscosity increase of the latex solutions.

Scheme 3.4: Chemical structure of an associative rheology modifier. The average relative amounts of each of the monomers in the chains (X, Y, and Z) are variable, depending on the starting conditions.



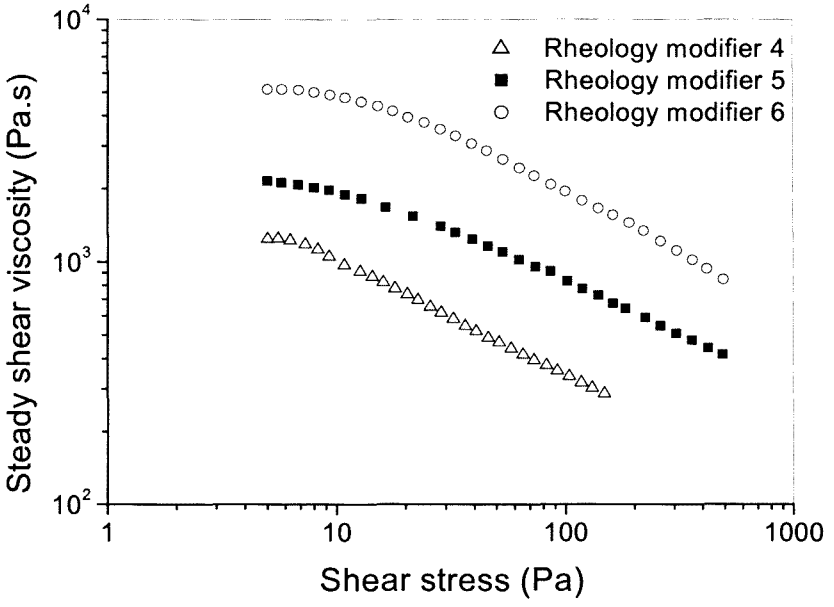


Figure 3.5: Steady shear viscosity of latex solutions thickened with associative rheology modifiers 4 – 6.

The specific rheology profiles given by the associative rheology modifiers are a direct result of the mutual interaction of the hydrophobic groups on the polymer with each other and with other hydrophobic components (latex particles) dispersed in the aqueous phase.[16] The dual thickening mechanism of the associative alkali-soluble rheology modifiers is described in Section 2.3.5.3.

Again a conceptual model with regard to the rheological observations may be appropriate. In this case one may correlate the observations with a simple model consisting of a linear combination of springs and dashpots. The dashpots may be equivalent to the hydrophobic interactions of the hydrophobes with each other and the latex particles. In this case one may expect both elastic storage attributes as well as viscous flow in combination. The resultant shear-thinning graphs show no sudden yield stress but, instead, a slow viscous yield as one would expect for a system containing dashpots.

Figure 3.6 shows the steady shear viscosity of the latex solutions containing rheology modifiers 2, 5 and 9. Rheology modifier 9 is also expected to be an associative rheology modifier because of the hydrophobic macromonomer incorporated into its polymer backbone. In contrast to associative RMs 4 – 6, RM 9 has only five ethylene oxide spacer

units between the hydrophobic end group and the polymer backbone. RM 9 shows a similar rheology profile to those of the conventional rheology modifiers, where there is a drop in viscosity at a critical yield stress. The short ethylene oxide spacer length restricts the hydrophobes from extending from the intramolecular hydrophobe-hydrophobe interaction domains and polymer coils, and thus restricts association with hydrophobes from other chains and latex particles. The yield stress is not quite as clearly defined as in the case of the conventional rheology modifiers. The broadening of the yield stress region suggests that there is a small degree of intermolecular interaction between the hydrophobes and latex particles and intermolecular chain association.

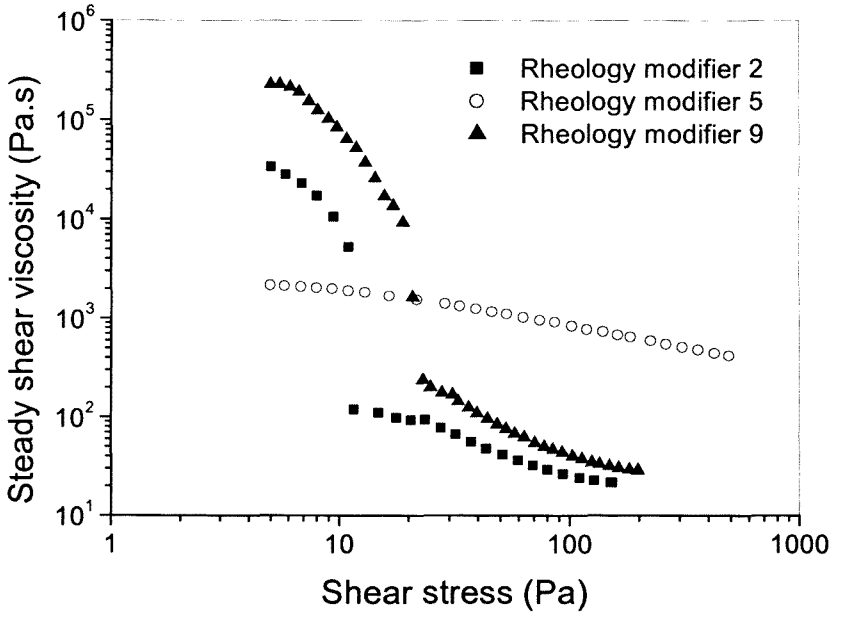


Figure 3.6: Steady shear viscosity of latex solutions thickened with polymers 2, 5 and 9.

3.3.2.3 Block copolymer

The rheology profile (Figure 3.7) of rheology modifier 7 (block A) shows similar behaviour to that of the other conventional rheology modifiers in Figure 3.4. In Figure 3.7 the latex solution thickened with rheology modifier 8 (AB block polymer) shows a similar rheology profile to that of the associative rheology modifiers in Figure 3.5. The addition of hydrophobic macromonomer 4 as a second block onto the polymer chain has a significant influence on the rheology profile of the latex solution thickened with this particular rheology modifier. The slope of the shear-thinning region of rheology modifier 8 is steeper than that of the other rheology modifiers in Figure 3.5. This is due to the associative hydrophobes being attached to only one end of the chain and not randomly distributed along the backbone, as in the case of the other associative rheology modifiers.

The steady shear viscosity of rheology modifiers 7 and 8 is approximately two orders of magnitude smaller than that of the other rheology modifiers. This is because the ratio of MMA/MAA (Table 3.3) was changed to enhance the effect that the hydrophobic macromonomer has on the rheology profile of the latex solutions.

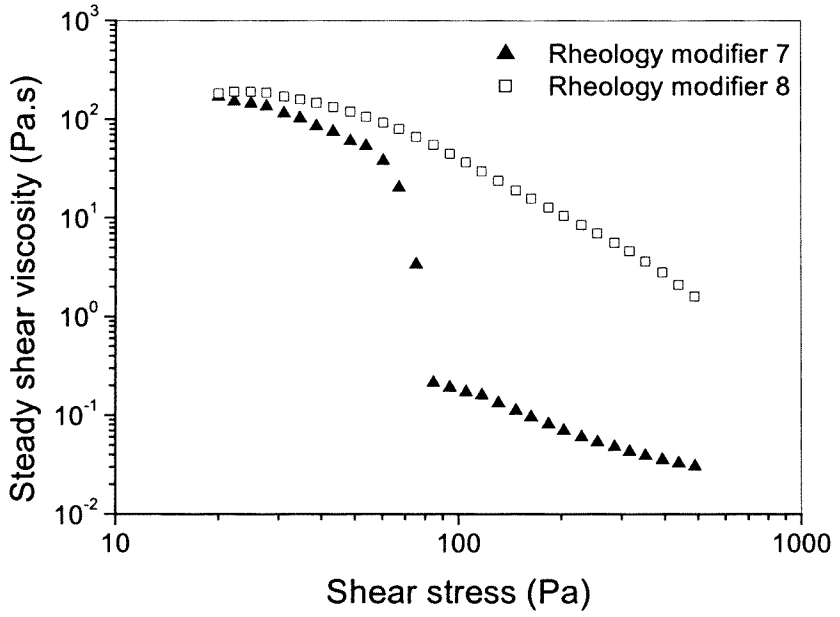


Figure 3.7: Steady shear viscosity of latex solutions thickened with polymers 7 and 8.

3.3.3 Dynamic properties

3.3.3.1 Conventional and associative rheology modifiers

All dynamic tests of the latex solutions thickened with the different rheology modifiers were conducted in the linear viscoelastic region of the latex solutions. Figure 3.8 shows a dominant G' (elastic effect) (see conceptual model on conventional rheology modifiers, section 3.3.2.1) over the entire frequency range for the latex solutions thickened with the conventional rheology modifier. In contrast to the previous graph, Figure 3.9 shows a dominant G" (viscous effect) (see conceptual model on associative rheology modifiers, section 3.3.2.2) over the entire frequency range. The latex solution thickened with the conventional rheology modifier behaves more like a gel or solid compared to the latex solutions thickened with the associative rheology modifier. The latexes thickened with the associative rheology modifier show viscous deformation, which is typical of a liquid.[17] The observed change in the dominant modulus can only be due to the hydrophobic interaction of the associative rheology modifiers that alters the dynamic properties of the latex solutions.

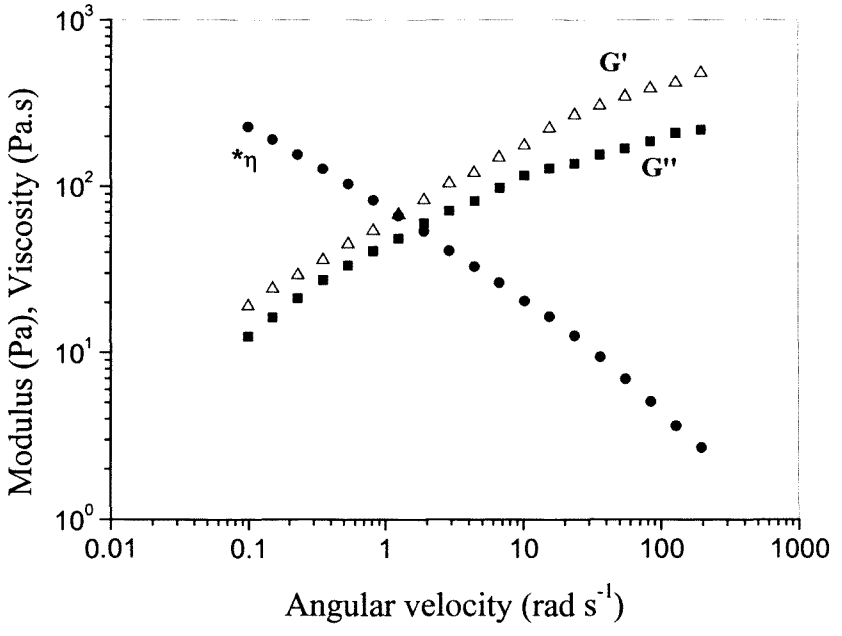


Figure 3.8: Storage and loss moduli and complex viscosity of latex solutions thickened with rheology modifier 2 (conventional polymer).

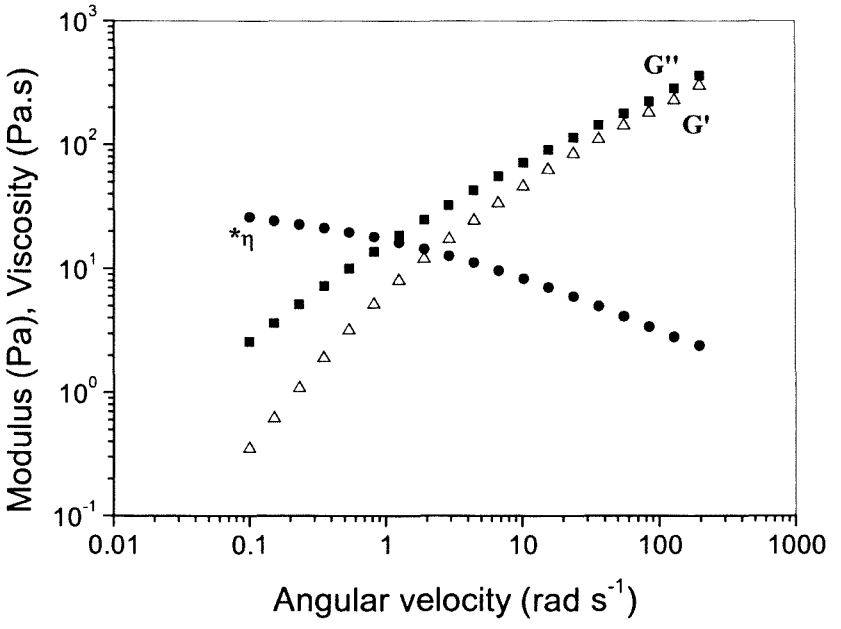


Figure 3.9: Storage and loss moduli and complex viscosity of latex solutions thickened with rheology modifier 5 (associative polymer).

Figure 3.10 shows the dynamic moduli for the latex solutions thickened with rheology modifier 9. Similar to what was observed in the case of the conventional rheology modifiers, a dominant G' (elastic effect) is observed. This confirms the steady shear viscosity data (Figure 3.6) implication that there is insufficient interaction between the associative hydrophobes and the latex particles.

A relative labile three-dimensional network is formed between the latex particles and the associative rheology modifiers compared to a more persistent three-dimensional network formed when the latex solution is thickened with conventional rheology modifiers. In the case of the labile three-dimensional network the intermolecular associations between the terminal hydrophobes and the latex particles are constantly broken and reformed. This explains the lack of a yield stress and the liquid-like behaviour that is observed for the associative rheology modifiers. In the case of the conventional rheology modifiers the persistent three-dimensional network (based on chain entanglement) is initially very strong (high low-shear viscosity values), but at a critical stress (yield stress) the three-

dimensional network is broken, which results in a dramatic drop in the viscosity and also explains the solid-like behaviour of the latex solutions.

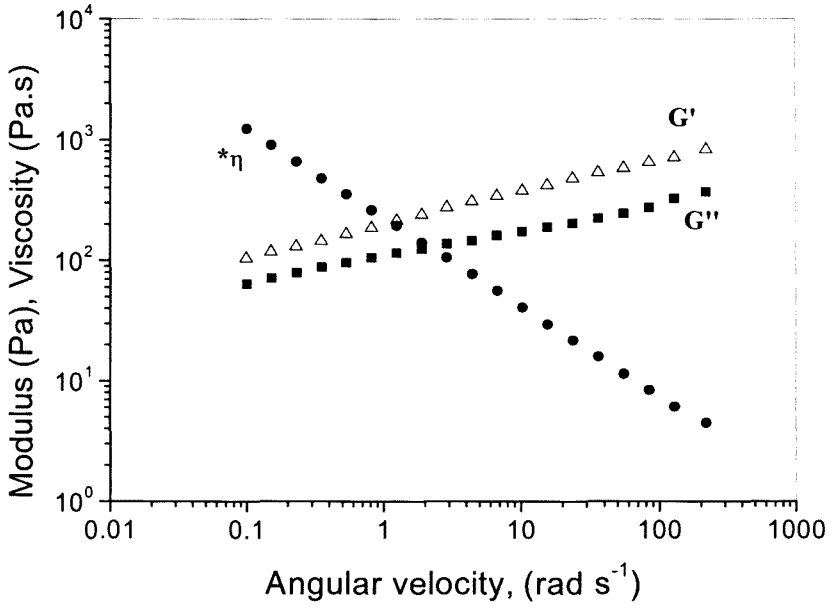


Figure 3.10: Storage and loss moduli and complex viscosity of the latex solutions thickened with rheology modifier 9 (associative polymer).

3.3.3.2 Block copolymer

Rheology modifier 7 (block A) is a conventional rheology modifier and therefore has the same dynamic modulus profiles (dominant G') as that of the conventional rheology modifier in Figure 3.8. In contrast to this, rheology modifier 8 (block AB) shows a crossover point between G' and G" at lower frequencies in Figure 3.11. This means that at lower frequencies the viscous effect is dominant over the elastic effect for this type of polymer. This change in the dynamic moduli profiles is a result of the addition of the associative macromonomers as a second block onto the conventional rheology modifier 7 (block A). The fact that G" is not dominant over the entire frequency range is probably due to the fact that the macromonomers are only attached to the one end of the polymer chains and not randomly distributed along the backbone. This confirms the steady shear data of rheology modifiers 7 and 8 in Figure 3.7.

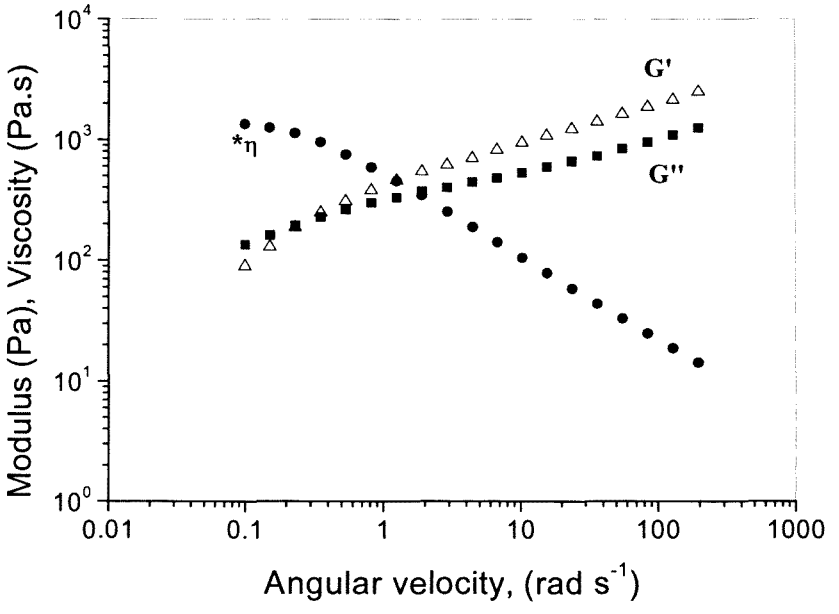


Figure 3.11: Storage and loss moduli and complex viscosity of the latex solutions thickened with rheology modifier 8 (associative block copolymer).

3.4 Conclusions

The synthesis of rheology modifiers with different molar masses, chemical compositions and chain end functionalities via the *in situ* RAFT solution reaction of AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate, methacrylic acid and hydrophobic macromonomers was successfully carried out. The free radical polymerisation reactions showed good living characteristics: well-controlled molar mass, controlled molar mass distribution, linear relationship between molar mass and monomer conversion and the ability to chain extend by forming an AB block copolymer.

The RAFT process made it possible to tailor-make the rheology modifiers. Each of the different types of rheology modifiers gave the latex solutions their own specific rheology profile. Although an increase in molar mass increases the viscosity, it has no major influence on the type of rheology profile of the latex solution. However, contrary to this, the addition of a macromonomer to the polymer chain has a major influence on the type of rheology profile observed. The influence of the macromonomers is further underlined

by the role the number of ethylene oxide spacer units play in the type of rheology profile that is observed for the latex solutions.

The latex solutions containing the conventional rheology modifiers had a more solid-like behaviour, in contrast to the associative rheology modifiers that gave the latex solutions a more liquid-like behaviour. Addition of the associative macromonomers (reaction 8) as the second block underlined the major influence they play in changing the rheology profiles, from a solid-like (conventional rheology modifiers) behaviour to liquid-like (associative rheology modifiers) behaviour, by forming intramolecular and intermolecular associations.

The associative rheology modifier 9 containing HM1 shows very contrasting steady shear viscosity and dynamic property results compared to the other associative rheology modifiers containing HM4. This is due to the short ethylene-oxide spacer length in HM1 that restricts the terminal hydrophobes from extending far enough into the latex matrix to form intermolecular associations with hydrophobes from other chains and latex particles.

The associative rheology modifier 8 (AB block copolymer) gives a similar steady shear viscosity profile to that of the associative rheology modifiers containing HM4, but the slope of the shear thinning region is steeper than that of the other associative rheology modifiers. Rheology modifier 8 shows a cross over point in the dynamic property results. It changes from being solid-like in behaviour at high frequencies to liquid-like in behaviour at low frequencies. This is due to the associative macromonomers being attached to only one end of the chain and not randomly distributed along the backbone, as is the case for the other associative rheology modifiers.

3.5 References

1 Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Bassett, D. R. *J. Polym. Sci., Part B: Polym. Phys.* 1998, 36, 2275.

2 Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* 2000, 33, 1727.

3 Tam, K. C.; Tiu, C. *J. Rheol.* 1989, 33, 257.

4 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 1426.

5 Shay, G. D. *Alkali-swellable and Alkali-Soluble Thickener Technology*, American Chemical Society, 1989, Chapter 25, p. 457.

6 Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.

7 Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. WO 98/01478*, 1998.

8 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.

9 Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.

10 Rizzardo, E.; Thang, T. H.; Moad, G. *PCT Int Appl WO 99/05099*, 1998.

11 Vosloo, J. J.; de Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* 2002, 35, 4894.

12 Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* 1999, 143, 291.

13 LeSota, S.; Lewndowski, E. W.; Schaller, E. J. *J. Coat. Technol.* 1989, 61, 135.

14 Vebrugge, G. D. *J. Appl. Polym. Sci.* 1970, 14, 897.

15 Shay, G. *Surf. Coat. Int.* 1993, 11, 446.

16 Tiu, C.; Nicolae, G.; Tam, K. C. *J. Polym. Res.* 1996, 3, 201.

17 Larson, R. G. *The Structure and Rheology of Complex Fluids*, Oxford University Press, 1999, 1.

CHAPTER 4

The Effects of Ethylene Oxide Chain Length on the Rheological Properties of Model Alkali-Soluble Rheology Modifiers Synthesised Using 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic Acid as RAFT Agent

Synopsis: *This chapter describes the rheological behaviour of conventional and associative rheology modifiers in alkali solution and in a well-characterised core-shell emulsion. The different associative rheology modifiers containing varying amounts of ethylene oxide spacer units, between the terminal hydrophobic group and the main chain, showed contrasting behaviour in alkali solution vs. emulsion solutions.*

The model alkali-soluble rheology modifiers were synthesised by the RAFT polymerisation of methyl methacrylate, methacrylic acid, and three different associative macromonomers, containing 20, 50 and 100 ethylene oxide spacer units. The polymers synthesised showed well-controlled molar mass and narrow molar mass distribution. The steady shear viscosity data for the core-shell emulsions, thickened with conventional and associative rheology modifiers, are well described by the Herschel-Bulkley and Carreau models respectively.

4.1 Introduction

Associative alkali-soluble rheology modifiers are usually terpolymers consisting of a carboxylic monomer, a hydrophobic monomer, and a third macromonomer that is associative. Variability within the macromonomer structure is obtained by altering the type of terminal hydrophobic group, type of ethylenic unsaturation, and size of the polyethoxylated or poly(ethoxylated-propoxylated) component.

The dual thickening mechanism of these associative rheology modifiers is described in Section 2.3.5.3. It is the addition of the hydrophobic macromonomers that is responsible for the enhanced thickening and unique rheological properties frequently observed in aqueous solutions and dispersed-phase systems containing these rheology modifiers.[1]

The use of the RAFT process as controlled free radical polymerisation technique it is possible to synthesis rheology modifiers of predetermined molar mass, narrow polydispersities, and tailored architecture.[2-5] This control over the architecture of the rheology modifier gives one the tool to determine the role each of the components in the rheology modifier plays. Understanding the role that each of the components play then enables one to modify the performance of the rheology modifier so that the specific rheological properties desired for the end products are obtained.

This chapter will focus on the number of ethylene oxide spacer units situated between the ethylenic unsaturation at one end of the macromonomer and the hydrophobic group at the other end and their effects on changing the performance of the rheology modifiers. This will be investigated in alkali-solution and in a well characterised core-shell emulsion.

4.2 Experimental

4.2.1 Reagents

Methyl methacrylate (MMA, 98%) and methacrylic acid (MAA, 98%) were obtained from Plascon Research centre, University of Stellenbosch. The MMA was washed with a 0.3 M solution of KOH and distilled under vacuum to remove the inhibitor. The nonylphenyl surfactants containing 20 (Berol 292, 99%, Akzo Nobel), 50 (Berol 291, 99%, Akzo Nobel) and 100 (Igepal-CO-990, 99%, Sigma-Aldrich) ethylene oxide units were used as received. 2,2-Azobisisobutyronotrile (AIBN, Delta Scientific, 98%) was used as received.

The following chemicals were used in the synthesis of the macromonomers and the RAFT agents: acryloyl chloride (Acros, 99%), bromobenzene (Fluka, 99%), carbon disulfide (Sigma-Aldrich, 99.9%), 33% HCl solution (Sigma-Aldrich), dimethyl sulfoxide (Unilab, Saarchem, 99.5%), 4,4-(azobis)-cyanovaleric acid (75% by weight + 25% water) and iodine crystals (Fluka). These reagents were used as received. THF (Burdick & Jackson, 99%) were dried before use. Magnesium turnings (Unilab) were used as received. All water used was distilled and passed through a Milli-Q (Millipore) ion exchange filtration system (DDI water).

4.2.2 Analyses

Size exclusion chromatography (SEC): The molar masses and molar mass distributions of the polymers were measured by size exclusion chromatography. The chromatograph used was a Waters 600E module with a Waters 410 differential refractometer. THF was used as mobile phase with a flow rate of 1.0 mL min^{-1} at a column temperature of 35 °C. Four Phenogel columns (300mm × 7.80mm) with respective pore sizes of 100, 10^3, 10^4 and 10^5 Å were used in series. The system was calibrated using six narrow molar mass PMMA standards, in the range of 2500 – 900 000 g mol^{-1}, supplied by Pressure Chemicals. Molar masses are reported as PMMA equivalents. Prior to SEC analysis, methacrylic acid groups were converted to methyl methacrylate units with tetramethylammonium hydroxide and methyl iodide in THF at 80 °C.[5]

^{1}H-NMR: All ^{1}H NMR spectra for the bis(thiobenzoyl) disulfide, 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, unreacted surfactants and the associative macromonomers were obtained using a Varian VXR 300 spectrometer operating at 300 MHz. All spectra obtained were calibrated using 0.05% TMS as the internal standard.

Rheology: The rheological analyses of the various samples were done with a Paar Physica MCR 300 rheometer, using a coaxial and a double gap measuring system. All rheological measurements were conducted at the same temperature of 25 °C. In the oscillatory experiments, the frequency sweep was carried out within the linear viscoelastic region.

Sample preparation and analysis:

SEC: Samples were prepared for SEC analysis by drying the polymer *in vacuo* and redissolving *ca.* 5 mg of the polymer in 1 mL THF. **^{1}H–NMR:** The macromonomer samples for the NMR analysis were prepared by dissolving 65 mg of the macromonomer in 0.65 mL of deuterated chloroform ($CDCl_3$) as solvent. **Viscosity profiles:** The rheological behaviour of the polymers was tested in a well-characterised core-shell emulsion with 46 wt% solids, an average particle size of 90 nm, pH 8.7 and T_g (DSC) of –5 °C. The core-shell polymer consisted of the following monomers and ratios. Core: methyl methacrylate (MMA, 80 wt %), butyl acrylate (BA, 17 wt %) and methacrylic acid (MAA, 3 wt %). Shell: butyl acrylate (BA, 63 wt %), methyl methacrylate (MMA, 31 wt %) and methacrylic acid (MAA, 3 wt %). The emulsion had a core:shell mass ratio of 5:2. The emulsion was diluted 50% by the addition of DDI water, and 3 wt % alkali-soluble thickener with respect to the undiluted emulsion was added. **Solution rheology:** Aqueous solutions having different polymer concentrations (5 and 10 wt % solutions) and the same pH (= 9) were prepared for the different rheology modifiers synthesised (Table 4.1). 2-Amino-2-methyl-1-propanol (AMP 95, 95% by weight + 5% water) was used to neutralise the polymer solutions until the pH reached the desired value.

4.2.3 Synthesis of hydrophobic macromonomers:

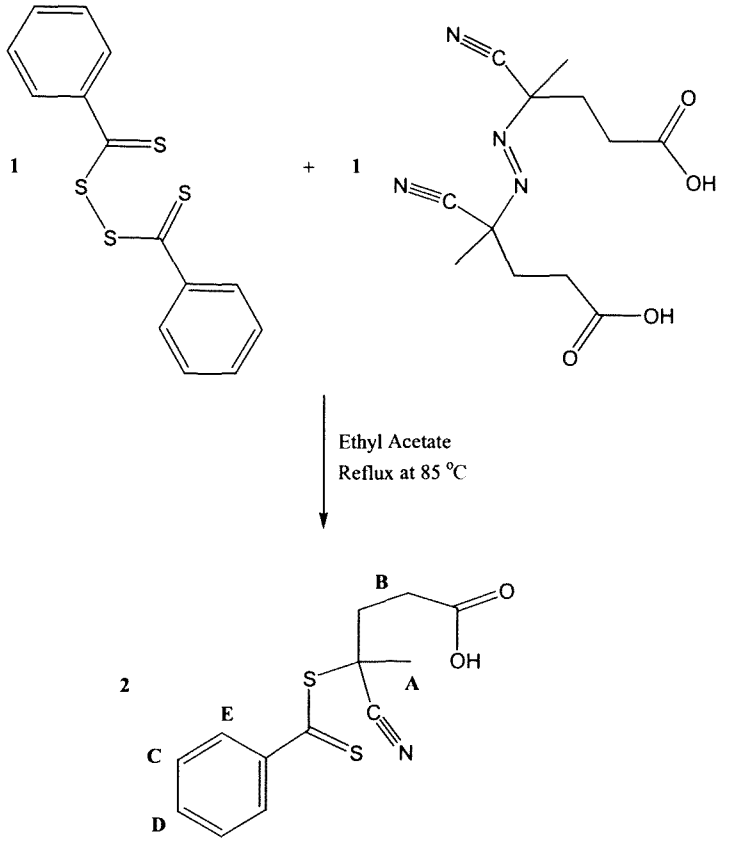
Three associative hydrophobic macromonomers, containing varying amounts of ethylene oxide spacer units, were synthesised as described in Section 3.2.3. The products, hydrophobic macromonomer two (HM 2, 20 ethylene oxide units, 12.62 g, 99% yield), hydrophobic macromonomer three (HM 3, 50 ethylene oxide units, 27.07 g, 99% yield) and hydrophobic macromonomer four (HM 4, 100 ethylene oxide units, 51.15 g, 99% yield, purity (^{1}H NMR) > 97 %), were obtained as white solid materials.

4.2.4 Synthesis and characterisation of 4-Cyano-4-((thiobenzoyl)sulfanyl) pentanoic acid

4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid was synthesised by reacting bis(thiobenzoyl) disulfide with 4,4'-azobis(4-cyanopentanoic acid). See the reaction schematic in Scheme 4.1. The synthesis of bis(thiobenzoyl) disulfide was based on the reaction of Rizzardo et al.[6] A detailed description of the process is given in Section 3.2.4. The product bis(thiobenzoyl) disulfide (15.61 g, 85 % yield, purity (^{1}H NMR) >90 %)) was obtained as red/purple-coloured crystals.

A solution of 4,4'-azobis(4-cyanopentanoic acid) (9.00 g, 0.0240 mol) and bis(thiobenzoyl) disulfide (7.00 g, 0.0229 mol) in ethyl acetate (300 mL) was heated to 85 °C and refluxed for 24 hours. The volatile organic components were removed *in vacuo* and the crude product was then purified by column chromatography (Kieselgel-60, 0.063 – 0.2 mm / 70 – 230 mesh) with a solution of ethyl acetate, *n*-pentane and heptane (4:3:3 mole ratio) as eluent, to give 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid as a red solid (7.85 g, 61 % yield, purity (^{1}H NMR) > 95 %). The ^{1}H NMR spectrum is shown in Figure A.8 of Appendix A and reveals the following peaks (see Scheme 4.1 for assignments), δ (ppm): 1.96 (s, 3H, **A**), 2.4-2.8 (m, 4H, **B**), 7.44 (m, 2H, **C**), 7.61 (m, 1H, **D**), 7.96 (d, 2H, **E**).

Scheme 4.1: The reaction schematic for the synthesis of 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid; the reaction of bis(thiobenzoyl) disulfide with 4,4'-azobis(4-cyanopentanoic acid).



4.2.5 Synthesis of conventional alkali-soluble thickeners

The conventional alkali-soluble thickeners were synthesised by the copolymerisation of methyl methacrylate and methacrylic acid in the presence of the RAFT agent 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid. Three copolymers with different molar masses were synthesised. The quantities of the different reagents used in the three reactions are shown in Table 4.1.

The general procedure for the three reactions was as follows: a reactor was charged with methanol (40 mL) and ethyl acetate (120 mL) and the monomers added. UHP grade nitrogen gas was bubbled through the reaction mixture for 30 min to remove oxygen. The initiator (AIBN) and the RAFT agent (4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid) were separately dissolved in the solvent (10 mL) and added to the reactor. The reaction

solution was heated to 80 °C and reacted for 16 hours. After the reaction was complete, the polymer solution was left to cool to room temperature. The polymer was then precipitated with *n*-pentane and dried under vacuum.

Table 4.1: Quantities of reagents used in the synthesis of the conventional rheology modifiers by the RAFT solution reaction of AIBN, 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, methyl methacrylate and methacrylic acid at 80 °C.

Expt	Methanol (mL)	Ethyl acetate (mL)	Methacrylic acid	Methyl methacrylate	RAFT agent	AIBN
1	40	120	25 g 0.290 mol	25 g 0.250 mol	0.4670 g 0.00167 mol	0.0910 g 0.00056 mol
2	40	120	25 g 0.290 mol	25 g 0.250 mol	0.2338 g 0.00084 mol	0.0455 g 0.00028 mol
3	40	120	25 g 0.290 mol	25 g 0.250 mol	0.1491 g 0.0005 mol	0.1491 g 0.0005 mol

4.2.6 Synthesis of alkali-soluble thickeners containing hydrophobic macromonomers:

Nine hydrophobically modified polymers with varying molar masses and chain architecture were synthesised by the method described above. These polymers contain the hydrophobic macromonomers HM 2, HM 3 and HM 4. Table 4.2 contains the quantities used in the syntheses of these rheology modifiers.

The amount of macromonomer incorporated into the polymer chains was determined by following the decrease in free macromonomer during polymerisation. This was achieved by recording ^{1}H NMR spectra (Figure 4.1) at time zero and time *t* (time at which polymerisation reaction is stopped). The decrease in the concentration of free macromonomer was calculated relative to an internal reference (trioxane), using the following equations:

$$[HM]_t = \frac{R_{(HM)_t}}{R_{(HM)_0}}[HM]_0 \qquad 4.1$$

with $$R_{(HM)_0} = \frac{\text{vinylic HM protons integral}}{\text{reference integral}} \quad \text{at time 0} \qquad 4.2$$

$$R_{(HM)_t} = \frac{\text{vinylic HM protons integral}}{\text{reference integral}} \quad \text{at time } t \qquad 4.3$$

It is expected that the macromonomer incorporation will be randomly distributed along the polymer chain.

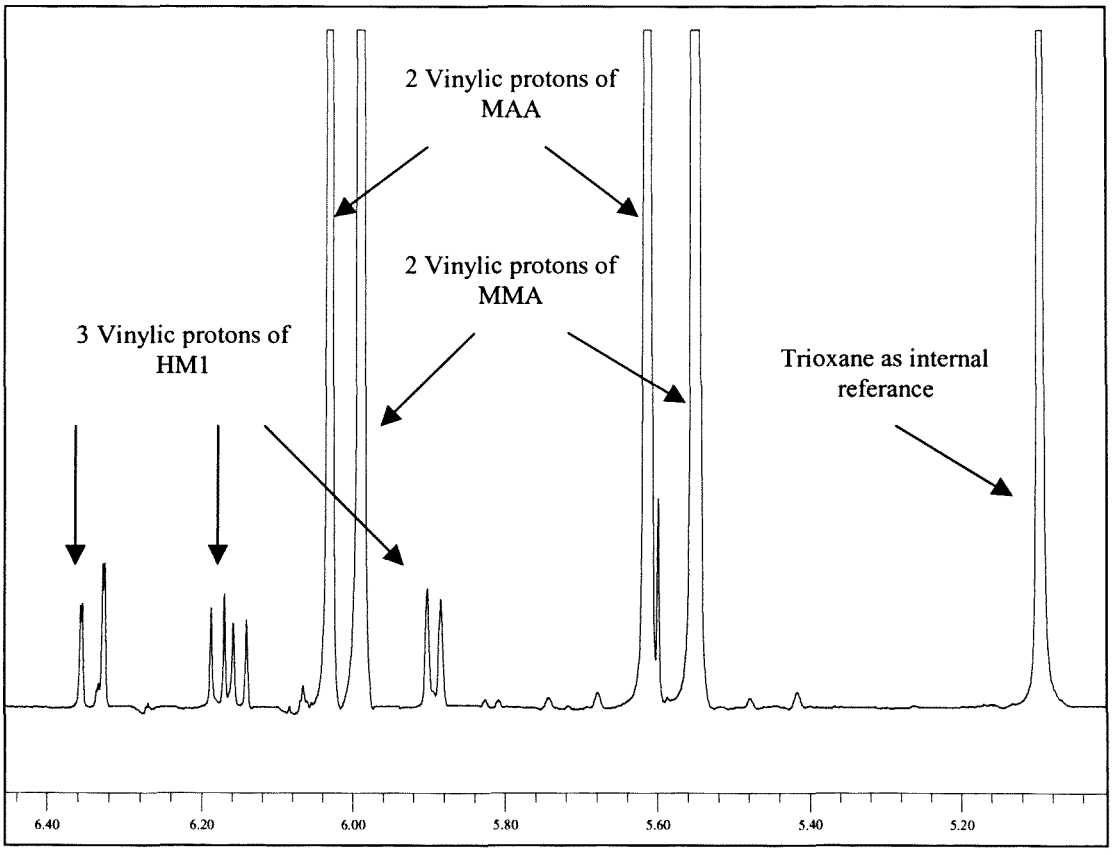


Figure 4.1: ^{1}H-NMR spectrum of the reaction mixture containing MMA, MAA, HM4 (trioxane as internal reference).

Table 4.2: Quantities of reagents used in the synthesis of the associative rheology modifiers by the RAFT solution reaction of AIBN, 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, methyl methacrylate, methacrylic acid and hydrophobic macromonomers at 80 °C.

Expt	Methanol (mL)	Ethyl acetate (mL)	MAA	MMA	HM	RAFT agent	AIBN
4	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM2) 6.23 g 0.0054 mol	0.4670 g 0.00167 mol	0.0910 g 0.00056 mol
5	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM2) 6.23 g 0.0054 mol	0.2338 g 0.00084 mol	0.0455 g 0.00028 mol
6	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM2) 6.23 g 0.0054 mol	0.1491 g 0.0005 mol	0.1491 g 0.0005 mol
7	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM3) 13.36 g 0.0054 mol	0.4670 g 0.00167 mol	0.0910 g 0.00056 mol
8	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM3) 13.36 g 0.0054 mol	0.2338 g 0.00084 mol	0.0455 g 0.00028 mol
9	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM3) 13.36 g 0.0054 mol	0.1491 g 0.0005 mol	0.1491 g 0.0005 mol
10	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM4) 25.24 g 0.0054 mol	0.4670 g 0.00167 mol	0.0910 g 0.00056 mol
11	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM4) 25.24 g 0.0054 mol	0.2338 g 0.00084 mol	0.0455 g 0.00028 mol
12	40	120	25 g 0.290 mol	25 g 0.250 mol	(HM4) 25.24 g 0.0054 mol	0.1491 g 0.0005 mol	0.1491 g 0.0005 mol

4.3 Results and discusssion

All RAFT polymerisation reactions carried out produced polymers of controlled molar mass and narrow polydispersity (< 1.5). The molar masses, polydispersities, and monomer ratios of the polymers formed in reactions 1 – 12 (referred to as rheology modifiers 1 – 12, respectively) are listed in Table 4.3.

Table 4.3 also contains the relative amounts of hydrophobic macromonomer (HM) units per polymer chain calculated from ^{1}H NMR spectra (with trioxane as internal reference). Changing the number of ethylene oxide spacer units does not significantly affect the number of macromonomers that were incorporated per chain

Table 4.3: The monomer ratios and SEC results for the polymerisation of the different rheology modifiers by the RAFT solution reaction of AIBN, 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, methyl methacrylate, methacrylic acid and hydrophobic macromonomers at 80 °C.

Reaction	Composition	Monomer ratio	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	HM per chain
1	MMA/MAA	50/50	23200	27900	1.20	-
2	MMA/MAA	50/50	41700	48400	1.16	-
3	MMA/MAA	50/50	50400	61500	1.22	-
4	MMA/MAA/HM2	49.5/49.5/1	23400	32600	1.39	2
5	MMA/MAA/HM2	49.5/49.5/1	34600	49100	1.42	4-5
6	MMA/MAA/HM2	49.5/49.5/1	42000	60100	1.43	7-8
7	MMA/MAA/HM3	49.5/49.5/1	22500	31800	1.41	2
8	MMA/MAA/HM3	49.5/49.5/1	31200	45000	1.44	4-5
9	MMA/MAA/HM3	49.5/49.5/1	41900	59900	1.43	7-8
10	MMA/MAA/HM4	49.5/49.5/1	18000	25800	1.43	2
11	MMA/MAA/HM4	49.5/49.5/1	26700	38400	1.44	4-5
12	MMA/MAA/HM4	49.5/49.5/1	34400	50200	1.46	7-8

4.3.1 Steady shear viscosity

Two different models were used to describe the rheology profiles of the latex solutions thickened with either the conventional rheology modifiers (Herschel-Bulkley model) or the associative rheology modifiers (Carreau model).

4.3.1.1 Conventional rheology modifiers

The chemical structure of the conventional rheology modifiers consists of a random copolymer of MMA and MAA. In these polymers that contain no strongly hydrophobic regions (i.e. macromonomers), there is no strong hydrophobe-hydrophobe association. The Herschel-Bulkley model was used to describe the flow curves of the latex solutions thickened with the conventional rheology modifiers of differing molar mass.

Herschel-Bulkley model

There are a number of rheological models that describe non-Newtonian fluids; two of the simplest of these are the Bingham and the Power law models.

The Bingham plastic model is characterised by a linear stress-rate curve that does not pass through the origin. A finite stress, the yield stress, must be applied to the fluid before flow occurs. Once the yield stress has been exceeded, the stress increases linearly with increasing shear rate. The slope of the linear portion of the curve is called the plastic viscosity. Such behaviour is often referred to as ideal plastic behaviour and fluids that conform to the Bingham model as "Bingham plastics". Bingham behaviour may be expressed as follows[7-9]:

$$\tau = \tau_0 + u_p \dot{\gamma} \qquad 4.4$$

where τ is the shear stress, τ_0 is the yield stress, $\dot{\gamma}$ is the shear rate, and u_p is the plastic viscosity.

For many fluids, the coefficient of viscosity is not a constant, but is a function of shear rate. Such fluids can often be modelled by means of a power law.[10]

$$\tau = K \dot{\gamma}^n \qquad 4.5$$

where K is the fluid "consistency index" and n is a power law index.

The yield stress in the power-law model is zero. The power-law exponent n, which is dimensionless, describes the departure of the fluid from Newtonian behaviour. If $n = 1$ the fluid is Newtonian. The fluid becomes more shear thinning as n decreases. Such fluids are often known as pseudoplastic. The converse situation is where $n > 1$ when the fluid is shear thickening and such fluids are known as dilatant. The fluid consistency index, K, can be linked to viscosity. High K values correspond to a high viscosity.

The Herschel-Bulkley model, a three-parameter model, combines the features of both models described above. It allows a yield stress with power law behaviour at higher stress levels and is written as:

$$\tau = \tau_0 + u_p \dot{\gamma}^n \qquad 4.6$$

Herschel-Bulkley fluids are materials that behave as rigid solids when local stress τ is lower than a finite yield stress τ_0, and flow as nonlinearly-viscous fluids for $\tau > \tau_0$.

The Herschel-Bulkley model was used to calculate the yield stress for the flow curves of the conventional thickeners measured in this study (e.g. Figure 4.2), and provided a good fit to all such data with an average error of less than 5 %. This specific model was chosen because it describes a flow curve which has a yield stress (Bingham) and the viscosity coefficient is a function of the shear rate (power law). The effect of the molar mass of the rheology modifiers was examined. Figure 4.3 shows the effects of molar mass on the yield stress. It is clear from Figure 4.3 that as the molar mass increases there is an increase in the yield stress of the latex solution. This is due to the higher degree of chain entanglement, because of the increasing length of the polymer chains.

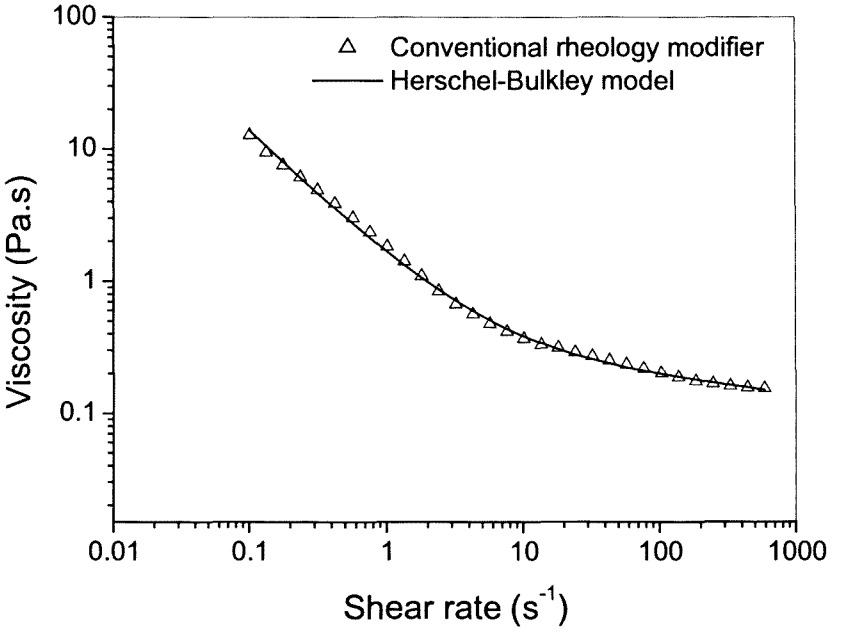


Figure 4.2: Herschel-Bulkley model fitted to the steady shear viscosity data of the latex solution thickened with a conventional rheology modifier 1.

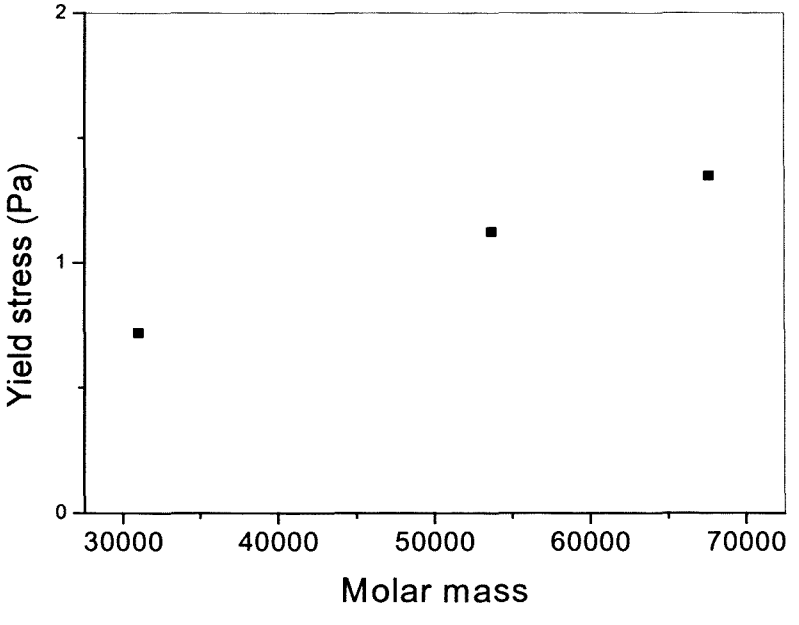


Figure 4.3: Effect of molar mass on the yield stress of the latex solution thickened with conventional rheology modifiers calculated from the Herschel-Bulkley model.

4.3.1.2 Associative rheology modifiers

The chemical structure of the associative rheology modifiers containing the hydrophobic macromonomers was shown in Scheme 3.4. The Carreau model was used to describe the flow curves of the latex solutions thickened by the different associative rheology modifiers.[11] Neither of the models in the previous section adequately describes the steady shear viscosity data of the latex solutions thickened with the associative rheology modifiers. In this section, two of the key parameters that control the relationship between polymer architecture and thickening efficiency were studied, i.e. molar mass of the polymer, and the number of ethylene oxide spacer units between the polymer backbone and the associative hydrophobic groups.

Figure 4.4 shows the Carreau model fitted to the rheology profile of a latex solution thickened with an associative rheology modifier. It provides a good fit to all such data with an average error of less than 5 %. The zero shear viscosity here is larger than the infinite shear viscosity. Many concentrated polymer solutions and melts display these characteristics. Phenomenological models are normally used to represent shear dependent viscosity data. The reason for this is that molecular models that describe dilute polymer solutions, like the Rouse[12] and Zimm[13] models, which assume linear viscoelastic behaviour, all predict a viscosity which is independent of shear rate and are therefore not valid for describing steady shear data.

Carreau model:

The Carreau equation describes the flow curve of a material with Newtonian regions at low and high shear rates and a shear-thinning region at medium shear rates.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda\dot{\gamma})^2]^{-N} \qquad 4.7$$

where η is the viscosity, η_0 is the zero shear viscosity, η_∞ is the infinite shear viscosity, $\dot{\gamma}$ is the shear rate, λ is the Carreau constant, and N is the Carreau exponent.

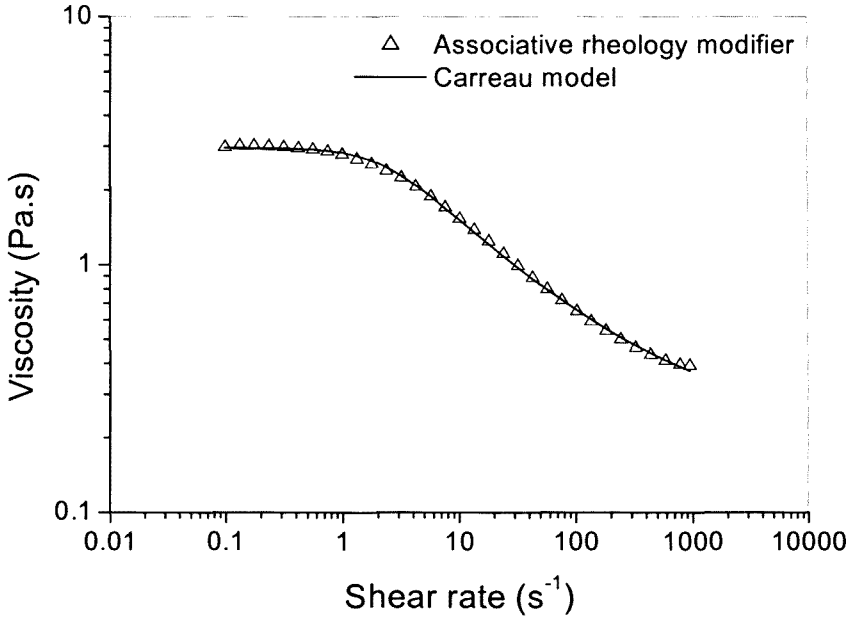


Figure 4.4: Carreau model fitted to the steady shear viscosity data of the latex solution thickened with an associative rheology modifier 4.

In many dilute aqueous polymer solutions, the infinite shear viscosity is much smaller than the zero shear viscosity, and often is ignored. The parameters N and λ are determined from the slope of the shear-dependent region and the reciprocal of the shear rate at which the tangents of the constant viscosity and shear dependent region intersect, respectively. It should be noted that although λ has the dimension of time it is not a true characteristic or relaxation time.

Figure 4.5 shows the influence of molar mass and ethylene oxide (EO) spacer length on the zero shear viscosity (calculated from equation 4.4) of the latex solutions thickened with associative rheology modifiers. It is clear that an increase in the molar mass increases the zero shear viscosity of the latex solutions. The increase in molar mass leads to longer chains, which leads to a greater number of chain entanglements and ultimately to higher viscosity. There is a drastic increase in the zero shear viscosity as the number of EO spacer units increases from 20 to 100 units. A larger number of EO spacer units allow the terminal hydrophobic groups to extend further into the latex matrix. This then leads to a bigger and stronger three dimensional network structure, which significantly increases the zero shear viscosity.

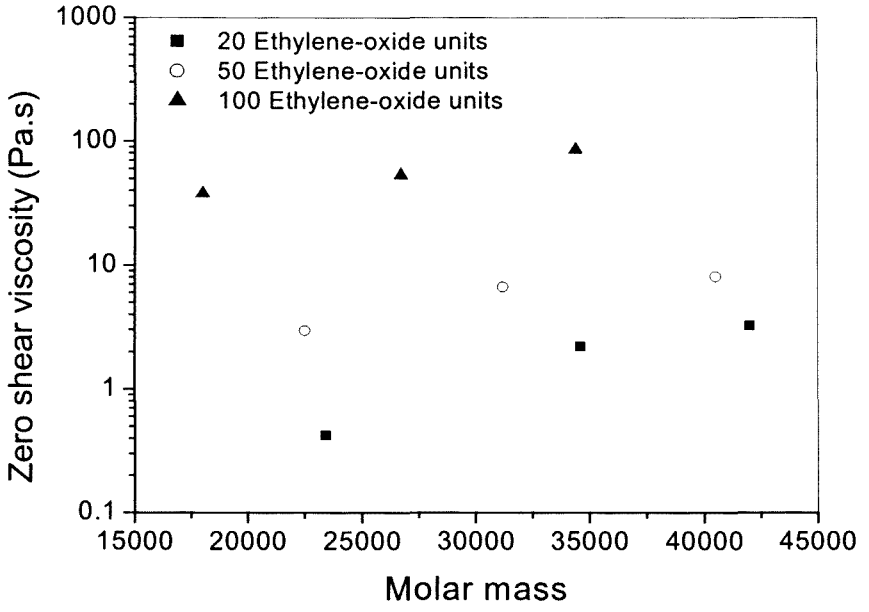


Figure 4.5: The effect of molar mass and ethylene oxide spacer length on the zero shear viscosity of the latex solution thickened with associative rheology modifiers calculated from the Carreau model.

4.3.2 Dynamic properties

All dynamic tests were conducted in the linear viscoelastic region of the latex solutions. Figures 4.6 – 4.8 show the dependence of storage (G') and loss (G") moduli on angular velocity (rad.s^{-1}) for a standard undiluted latex and for two latex solutions thickened by conventional and associative rheology modifiers respectively.

Figure 4.6 (undiluted latex) shows a dominant storage modulus at high frequency with a crossover point between the G' and G" at lower frequency. In Figure 4.7 (latex solution thickened with a conventional rheology modifier) the storage modulus (G') is dominant over the entire frequency range. To describe these observations in terms of a simple conceptual model, the conventional rheology modifiers can be considered to be analogous to a simple system of connected springs in which each polymer molecule can be thought of as a member of the ensemble of connected springs. The spring constant may be related to the molar mass of the polymer molecules. As for a system of connected springs, the energy introduced into the system by the applied stress will be stored so that once the applied stress is removed the spring can return to its original state. For this

reason, the latex solutions thickened with the conventional rheology modifiers show a dominant storage modulus and are solid-like in their rheological behaviour.

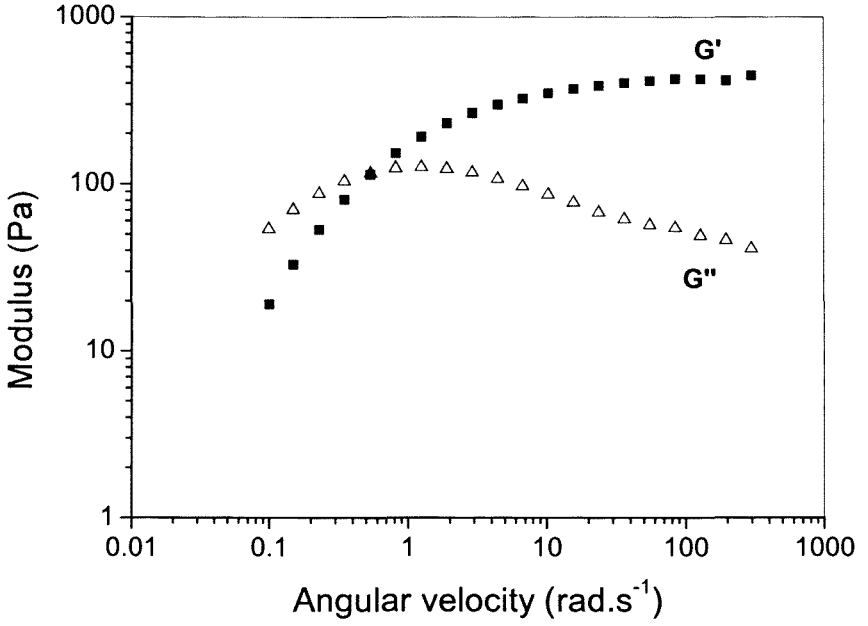


Figure 4.6: Storage and loss moduli of the undiluted latex. The latex is a well-characterized core-shell emulsion with 46 wt% solids, an average particle size of 90 nm, pH 8.7 and T_g (DSC) of –5 °C.

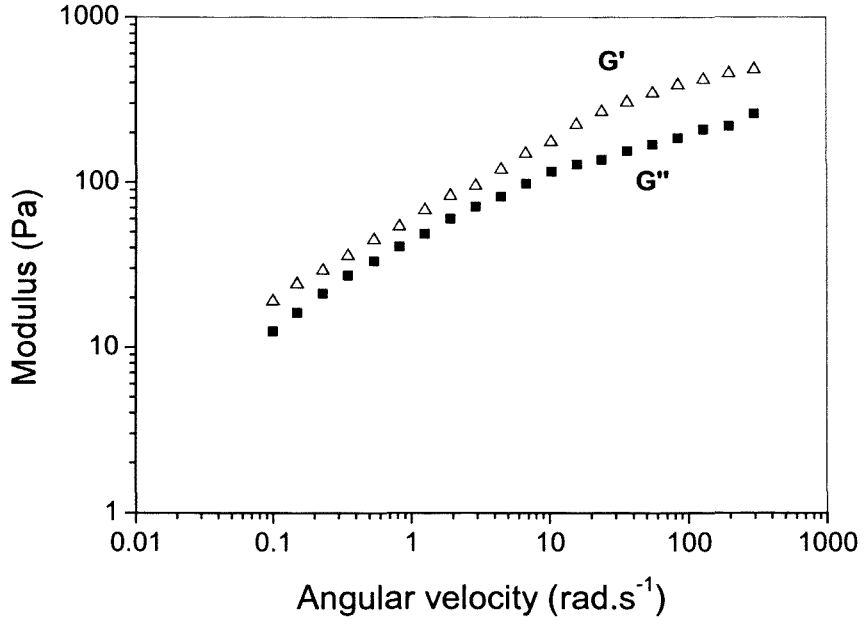


Figure 4.7: Storage and loss moduli of the latex solution thickened with conventional rheology modifier 2.

In contrast to the previous two graphs, Figure 4.8 (latex solution thickened with an associative rheology modifier) shows a dominant loss modulus (G") over the entire frequency range. The latex solution thickened with the conventional rheology modifier shows a more solid (gel)-like behaviour in comparison to the latex solutions thickened with the associative rheology modifiers, which show liquid-like behaviour. Once again, a conceptual model with regard to the rheological observations may be appropriate. In this case one may correlate the observations with a simple model consisting of a linear combination of springs and dashpots. The dashpots are considered to be equivalent to the hydrophobic interactions of the hydrophobic groups with each other and the latex particles. In this case one may expect both elastic storage attributes and viscous flow in combination. The majority of the energy introduced into the system by the applied stress is lost through the viscous flow of the dashpots.

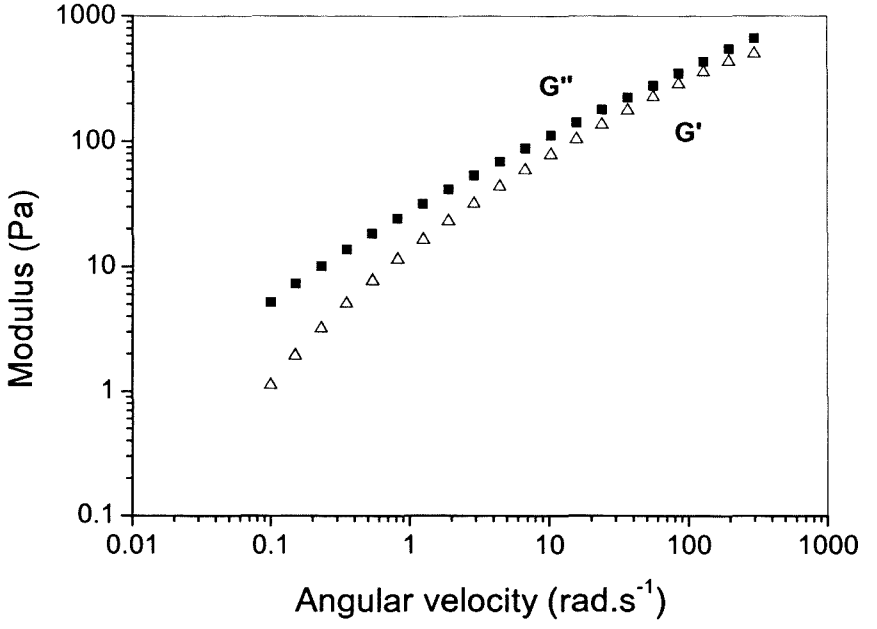


Figure 4.8: Storage and loss moduli of the latex solution thickened with associative rheology modifier 5.

As explained earlier for the associative thickening mechanism, the hydrophobic groups are considered to be the primary interactive components. So, although both elastic and viscous flow effects are present, the viscous contribution is dominant. This explains why the latex solutions thickened with the associative rheology modifiers show a dominant loss modulus and are therefore liquid-like in their rheological behaviour. The change of

the dominant modulus can only be due to the hydrophobic interaction of the associative rheology modifiers that alters the dynamic properties of the latex solutions. The conventional rheology modifiers have a different influence on the dynamic properties of the latex solutions because they merely thicken the aqueous phase by hydrodynamic volume effects and molecular chain entanglement.

4.3.3 Solution rheology

4.3.3.1 Effect of concentration

Figure 4.9 shows that the steady shear viscosity of an associative rheology modifier solution is approximately constant over the entire shear stress range measured (Newtonian behaviour). Similar results are observed for the conventional rheology modifier solutions. An increase in concentration leads to higher chain density, which leads to higher chain entanglement, which ultimately leads to an increase in viscosity. The Newtonian behaviour of the conventional and associative rheology modifier solutions are in contrast to the shear thinning behaviour of the latex solutions thickened with both types of rheology modifiers.

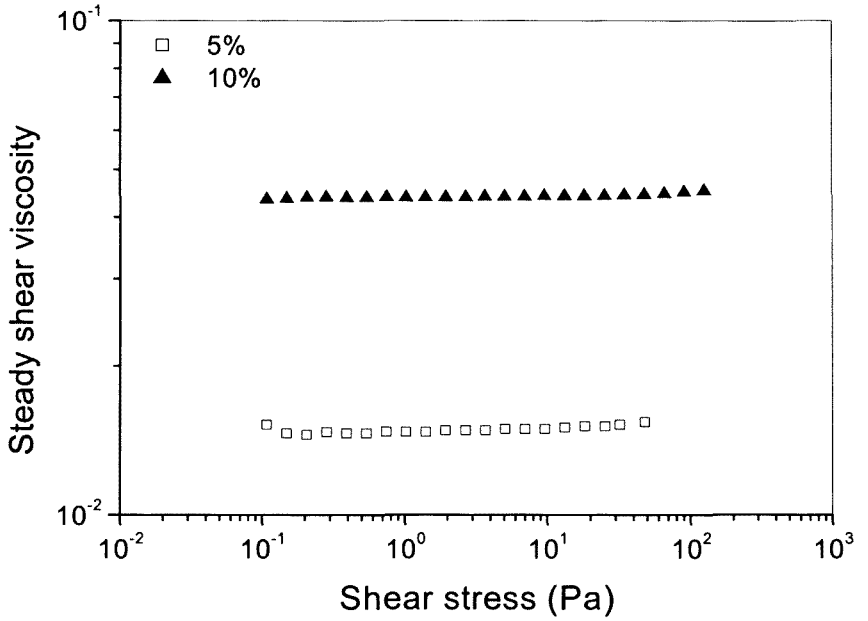


Figure 4.9: Steady shear viscosity of various polymer concentrations at pH 9 for rheology modifier 8.

Figure 4.10 displays the dynamic properties of two polymer concentrations at pH 9 for rheology modifier 8 (associative) in the absence of the latex solution. Similar results are seen for the rest of the associative and conventional polymer solutions where the loss modulus is higher than the storage modulus by several orders of magnitude. All the polymer solutions followed the usual behaviour of the majority of entangled polymeric systems reported in the literature, where all the flow curves appear to be parallel, even for the most concentrated solutions.

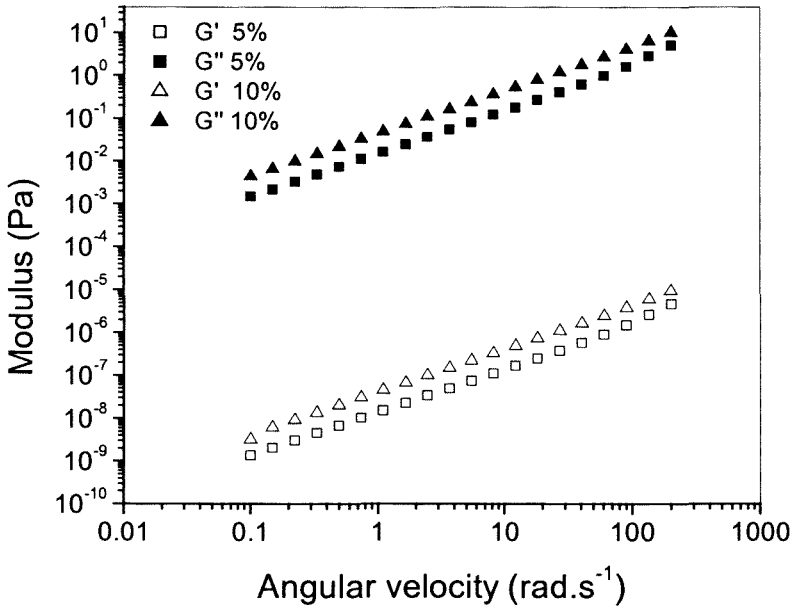


Figure 4.10: Dynamic properties at various polymer concentrations at pH 9 for rheology modifier 8.

4.3.3.2 The effect of the molar mass

Figure 4.11 shows that with an increase in molar mass there is an increase in the steady shear viscosity. The increase in polymer chain length leads to increased chain entanglements, which results in the higher viscosity. These results are seen for all of the rheology modifiers.

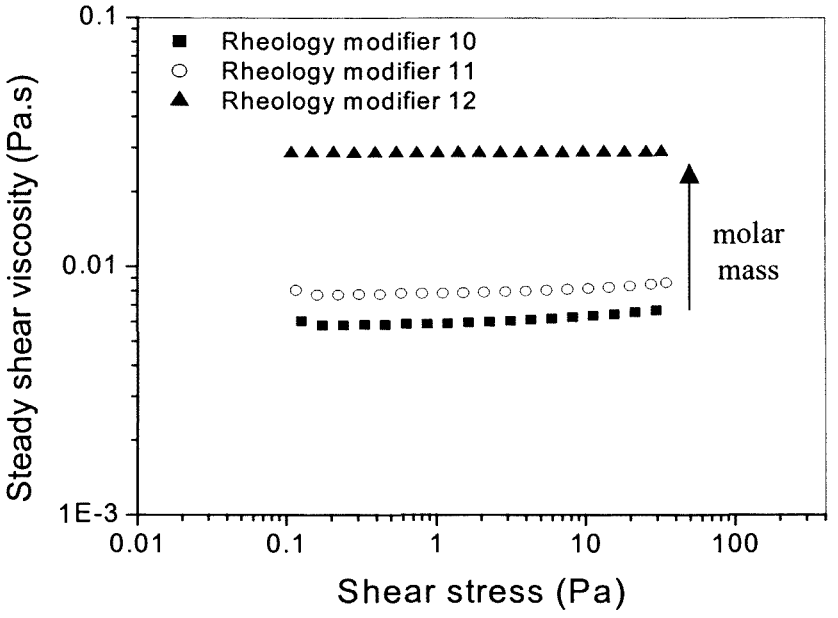


Figure 4.11: The steady shear viscosity data for the 5 % polymer solutions of rheology modifiers 10, 11 and 12.

4.3.3.3 The effects of varying the number of ethylene oxide spacer units in the rheology modifiers

Varying the number of ethylene oxide spacer units in the rheology modifiers has a significant effect on the solution rheology. Figures 4.12 – 4.14 illustrate the effects of the number of ethylene oxide spacer units have on the 5 % polymer solutions of RMs 5, 8 and 11. It is clear that the thickening efficiency is dependent on the number of ethylene oxide units in the macromonomers. It appears that the highest viscosity and dynamic properties are obtained for the rheology modifiers containing 50 ethylene oxide spacer units. The ethylene oxide spacer has two main functions, the first of which is to give flexibility to the hydrophobic groups. This provides the opportunity for the hydrophobic groups to come into contact with other hydrophobic groups on the same polymer chain (intramolecular) or on different polymer chains (intermolecular). The second function of the ethylene oxide spacer is that it changes the hydrophobicity of the macromonomer because it is hydrophilic in nature. It is obvious that with an increase in the number of ethylene oxide spacer units, the hydrophobicity of the macromonomer will be lower. The

associative network structures of the polymers in solution will be affected by both of these factors, and in order to obtain the desired thickening efficiency an optimal balance between the two is crucial.

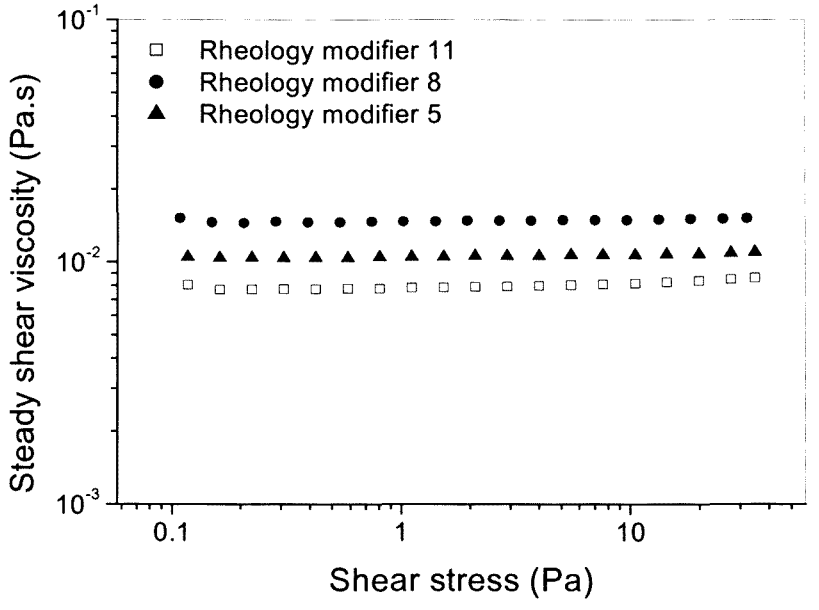


Figure 4.12: Steady shear viscosity data for the 5 % polymer solutions of rheology modifiers 5 (20 units), 8 (50 units) and 11 (100 units) containing varying numbers of ethylene oxide spacer units.

Although rheology modifier 11 contains the highest number of ethylene oxide spacer units in the polymer chains, it has the lowest steady shear viscosity (Figure 4.12) and lowest dynamic moduli (Figures 4.13 and 4.14). A higher number of ethylene oxide spacer units in the macromonomer will increase the probability of the latter forming intramolecular associations because the hydrophobic groups can then extend to a greater distance and associate with hydrophobic groups on the same polymer chain. By forming a larger number of intramolecular associations the polymer will tend to coil into a more compact conformation, which will lead to a reduction in the viscosity.

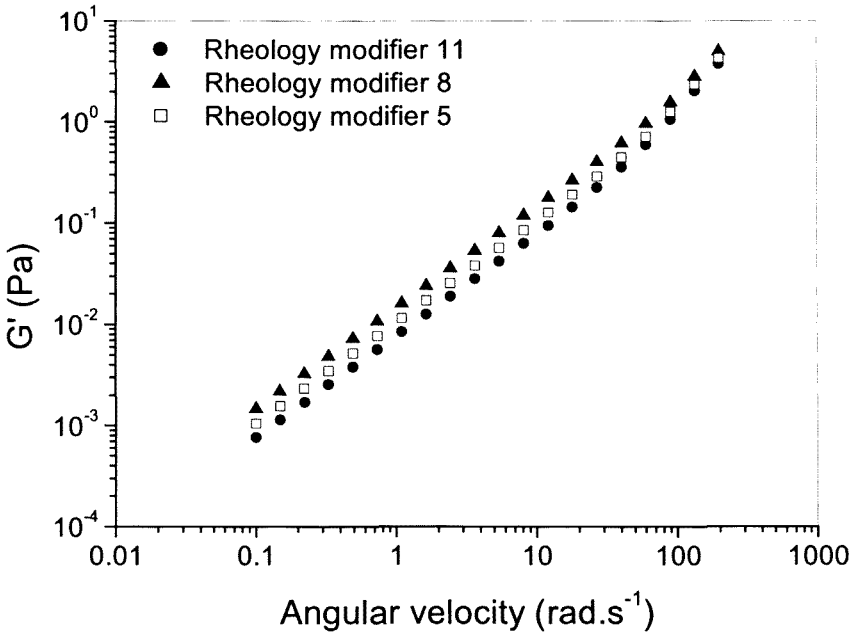


Figure 4.13: Storage modulus data for the 5 % polymer solutions of rheology modifiers 5 (20 units), 8 (50 units) and 11 (100 units) containing varying numbers of ethylene oxide spacer units.

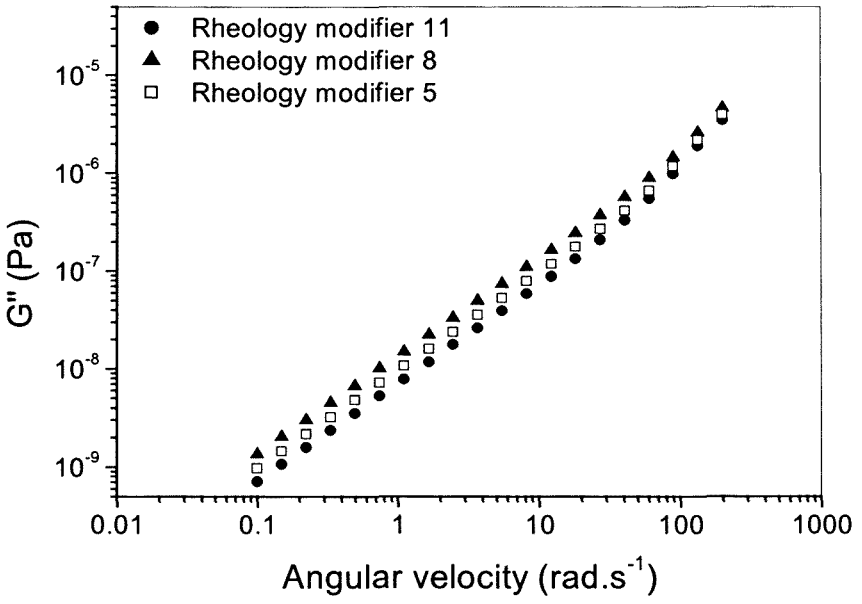


Figure 4.14: Loss modulus data for the 5 % polymer solutions of rheology modifiers 5 (20 units), 8 (50 units) and 11 (100 units) containing varying numbers of ethylene oxide spacer units.

Contrasting behaviour was observed when the alkali-soluble associative rheology modifiers were tested in solution compared to the results obtained when tested in a latex solution. The rheology results obtained from testing the associative rheology modifiers in the emulsion system shows clearly that the polymers containing the macromonomers with the longest ethylene oxide spacer units gave the highest viscosities (Figure 4.5). This could be attributed to the ability of the terminal hydrophobic groups to extend further into the latex matrix to form a bigger and stronger three-dimensional network. Contrary to this, the rheology modifiers in solution gave the highest viscosity for the polymers containing the macromonomers with 50 ethylene oxide spacer units. The polymers containing the macromonomers with the longest (100 units) ethylene oxide spacer units gave the lowest viscosity results in solution. As explained previously, it is probable that longer ethylene oxide spacer units lead to a higher probability of forming intramolecular associations, which would then lead to a reduction in viscosity.

A possible reason for the contrasting rheology behaviour is a result of the terminal hydrophobic groups on the rheology modifiers forming a stronger and/or preferable association with the latex particles rather than with other hydrophobic groups, on the same polymer chain (intramolecular) or other polymer chains (intermolecular). In solution, the only possible association that the terminal hydrophobic groups can form is with other hydrophobic groups on the same chain or on other polymer chains, since no latex particles are present.

4.4 Conclusions

Model alkali-soluble rheology modifiers with different molar masses and chemical compositions were successfully synthesised by the RAFT solution polymerisation of AIBN, 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, MMA, MAA and hydrophobic macromonomers containing varying numbers of ethylene oxide spacer units. The synthesised polymers showed well-controlled molar mass and narrow molar mass distribution.

The influence of molar mass on the performance of the rheology modifiers was strong in both the latex and alkali solutions. Increasing molar mass led to an increase in the viscosity due to the longer chains increasing chain entanglement. The addition of a

hydrophobic macromonomer gave two very different types of rheology profiles for the latex solutions thickened with the conventional rheology modifiers (Herschel-Bulkley model) and the associative rheology modifiers (Carreau model). The number of ethylene oxide spacer units between the terminal hydrophobic groups and the polymer backbone played a much greater role in the performance of the rheology modifiers than did the molar mass. The zero shear viscosity data of the latex solutions thickened with the different associative rheology modifiers showed a drastic increase in the viscosity as the number of ethylene oxide spacer units was increased from 20 to 100. In contrast to these observations, the polymer solutions (in the absence of latex) containing the rheology modifiers with the highest number of ethylene oxide spacer units gave the lowest viscosity, and the rheology modifiers containing 50 ethylene oxide units gave the highest viscosity.

It is suggested that the contrasting rheological behaviour (latex vs. solution) could be due to the preferable and/or stronger association of the terminal hydrophobes with the latex particles than with other terminal hydrophobic groups.

4.5 References

1 Thiebeault, J. C.; Sperry, P. R.; Schaller, E. J. *Proc ACS Div Polym Mater Sci Eng* 1984, 51, 353.

2 Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.

3 Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. WO 98/01478*, 1998.

4 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.

5 Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.

6 Rizzardo, E.; Thang, T. H.; Moad, G. *PCT Int Appl WO 99/05099*, 1998.

7 Friend, J. P.; Hunter, R. J. *J. Colloid Interface Sci.* 1971, 37, 548.

8 Uejima, H. *J. Appl. Phys.* 1972, 11, 319.

9 Klingenberg, D. J.; Zukoski, C. F. *Langmuir* 1990, 6, 15.

10 Abdel-Khalik, S. I.; Hassager, O.; Bird, R. B. *Polym. Eng. Sci.* 1974, 14, 859.

11 Carreau, P. J. *Transactions of the Society of Rheology* 1972, 16, 99.

12 Rouse, P. E. *J. Chem. Phys.* 1953, 21, 1272.

13 Zimm, B. H. *J. Chem. Phys.* 1956, 24, 269.

CHAPTER 5

Characterisation and Rheological Properties of Model Alkali-Soluble Rheology Modifiers Synthesised in Miniemulsion

Synopsis: *Conventional and associative alkali-soluble rheology modifiers have been successfully synthesised by the RAFT polymerisation of MMA, MAA and a hydrophobic macromonomer in miniemulsion. The effect that different types of initiators (water-soluble and oil-soluble) have on the polymerisation reactions was investigated. The KPS (water-soluble) initiated polymerisation reactions showed much faster polymerisation rates than the AIBN (oil-soluble) initiated systems. Further, a decrease in the percentage of MAA used in the miniemulsion systems led to a decrease in the rate of the polymerisation reactions.*

The rheology profiles of latex solutions thickened with the conventional rheology modifiers showed a significant drop in the viscosity at a critical shear stress (yield stress). This behaviour was not observed when the associative rheology modifiers were used, where no drop in viscosity occurred over the measured shear stress range. As the amount of hydrophobic macromonomer was increased from 1% to 5%, the dynamic properties of the latex solutions thickened with the associative rheology modifiers changed from more liquid-like (dominant G") to more solid-like (dominant G') in their behaviour.

5.1 Introduction

Free radical emulsion polymerisation is used extensively in industry to synthesise a wide range of products such as latex paints, paper coatings, textile coatings and speciality products such as rheology modifiers, cement additives and biomedical latexes. The absence of organic solvents and the compartmentalisation of the reaction give rise to the numerous advantages of the emulsion process. Water (inert and harmless), as continuous phase, provides a good medium for the removal of the heat of reaction and guarantees a product (i.e. latex) that has a relatively low viscosity and is easy to handle. Free radical emulsion polymerisation systems are relatively economical and robust, with a low sensitivity to impurities.[1,2]

The polymerisation reaction actually takes place in the latex particles that act somewhat like numerous bulk microreactors for polymerisation. Other advantages of the emulsion process include the ability to produce high molar mass polymers at a polymerisation rate higher than that of homogeneous systems. The amount of residual monomer is minimised because the polymerisation can usually be carried out up to very high conversion.

The ability to control the micro- and macrostructure of polymers synthesised by emulsion polymerisation processes will lead to the development of better products and expand the range of products available. One way of obtaining control over the structure of the polymers is by conducting living free radical polymerisation in a heterogeneous medium. This will allow one to synthesise polymers of controlled molar mass, narrow molar mass distribution and tailored chain architectures. The main approach in this chapter will aim to combine the best features of both emulsion and living free radical polymerisation to produce alkali-soluble rheology modifiers of controlled molar mass and chain architecture.

Several living polymerisation processes have already been successfully carried out in heterogeneous (with one of the phases being water) systems, e.g. nitroxide mediated polymerisation,[3-7] atom transfer living polymerisation (ATRP),[8-11] degenerative transfer,[12-14] and reversible addition-fragmentation chain transfer (RAFT) polymerisation.[15-20]

This chapter describes the synthesis of model alkali-soluble rheology modifiers using the RAFT process in miniemulsion. The effects that the type of initiator used (oil- or water-soluble) has on the miniemulsion polymerisation reactions will be investigated, along with the influence of the MMA:MAA ratio. Associative rheology modifiers containing different amounts of hydrophobic macromonomers were also synthesised, and their specific rheological properties measured.

5.1.1 Conventional emulsions (macroemulsions)

A typical *ab initio* emulsion polymerisation process is described as a three interval process (Scheme 5.1).[1,2] The reaction commences in *Interval I* (particle nucleation) and the initial reaction mixture normally consists of water, monomer(s), surfactant and initiator. Initially, the water-soluble initiator is dissolved in the continuous water phase and the monomer is emulsified by agitation. Most of the monomer is present in the form of monomer droplets stabilised by surfactant, while a small portion of the monomer is dissolved in the water phase. A large number of micelles are present in the water phase, formed by the remainder of the surfactant that is dissolved in the aqueous phase above the critical micelle concentration (cmc). Dissociation of the initiator leads to the formation of radicals that react with monomer dissolved in the water phase, to form oligomeric radicals. The incorporation of monomer units into oligomeric radicals growing in the water phase is limited by a critical degree of polymerisation, z, above which the growing polymer chain becomes surface active. At this point, the oligomeric radical will enter a micelle, swollen with monomer. For micellar entry the relative amounts are dependent on the rates of entry into existing micelles, which is dependant on their number and surface area.

In the early stages there is often competition between micellar entry, homogeneous nucleation and entry into growing particles. Emulsion polymerisation reactions can also be carried out below the cmc of the surfactant concentration and in surfactant free systems. Homogeneous nucleation becomes the predominant particle nucleation mechanism in the case of low surfactant concentration or surfactant free emulsions. The mechanism of homogeneous nucleation will be described in more detail in section 5.1.2.

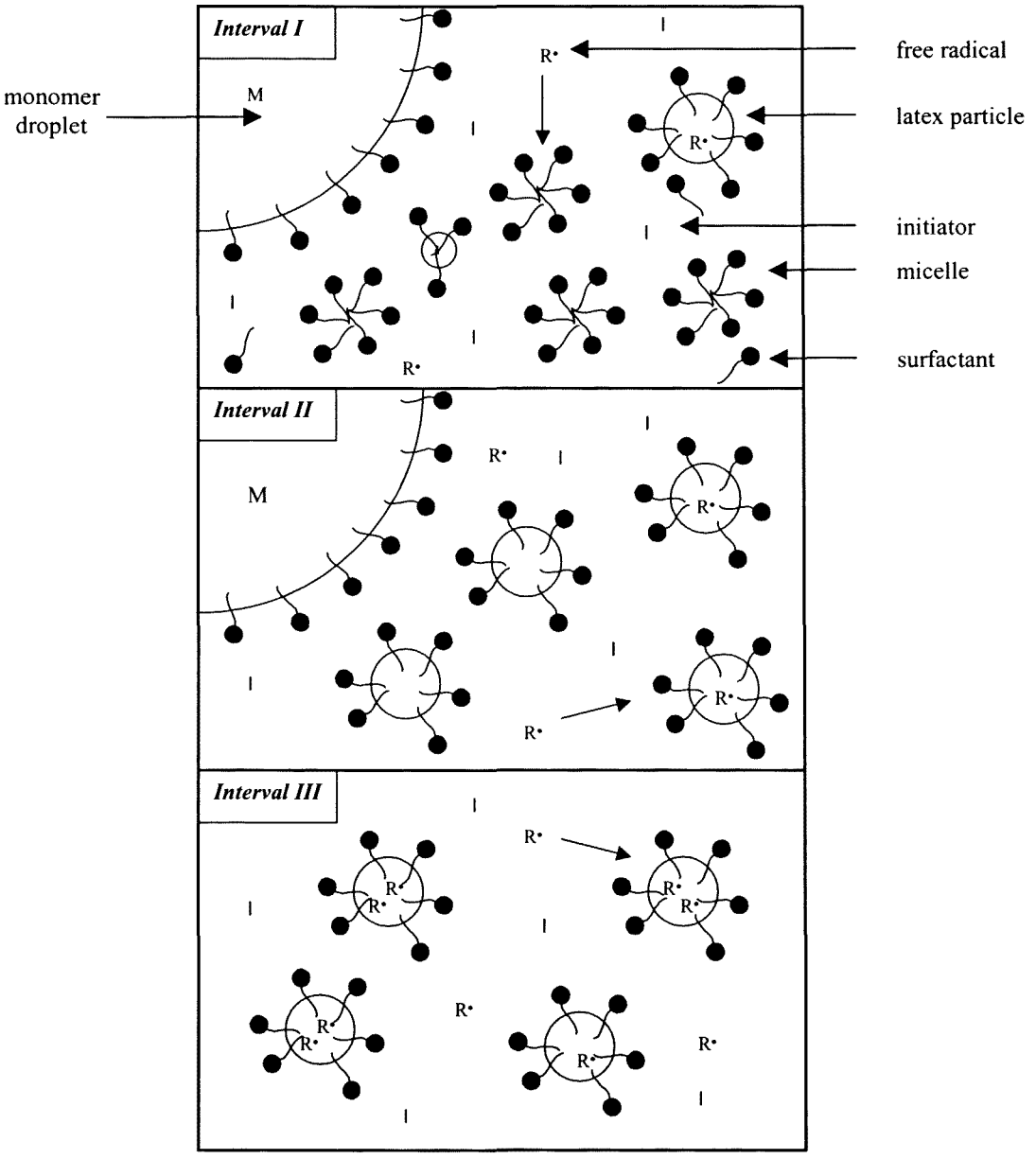
The radical entry into monomer droplets is usually neglected because of the very low surface area of the monomer droplets in comparison to that of the micelles. Monomer is consumed as the radical continues to grow, and is replenished by diffusion from the droplets, through the water phase, into the growing particle. During *Interval I,* new particles are continuously formed from micelles (and other processes), increasing the number of polymerisation sites and the polymerisation rate. The polymer particles continue to grow and absorb an increasing amount of surfactant onto their interface. This causes the number of micelles to decrease, since micelles are dynamic entities that can quickly disappear if the surfactant is consumed elsewhere. As this process continues a point will be reached where all the micelles have disappeared and the formation of new particles has essentially stopped, although it is still possible to form particles by either droplet entry (rare in true emulsion) or homogeneous nucleation.

Interval II commences once all particle formation has ceased and is characterised by a constant number of particles equal to the value reached at the end of *Interval I* (assuming no loss due to coagulation).

At the polymerisation sites (inside the particles), the concentration of monomer remains approximately constant as monomer is supplied from the monomer droplets to the particles at the same rate at which it is consumed. The result of a constant number of particles, a constant concentration of monomer inside the particles and a constant number of propagating radicals per particle leads to the polymerisation rate also remaining constant.

Interval III commences once all of the monomer droplets have disappeared. The remaining monomer is present inside the particles and while polymerisation continues, the rate decreases as the monomer concentration in the particle gradually decreases.

Scheme 5.1: The three intervals of an *ab initio* emulsion polymerisation.



There are several kinetic events that occur during emulsion polymerisation that are associated with chain growth. The initiator derived radicals propagate in the water phase to form short oligomeric radicals that can undergo termination or enter a particle. The critical chain length, z, at which the radical becomes surface active, is dependent on the type of monomer(s) and the oligomeric end group.[21] Once the z-meric radical has entered a particle, the radical will either terminate an already existing radical (assuming zero-one

kinetics) or continue growing until it is terminated by a second incoming radical or until transfer takes place to either the monomer or a transfer agent. The short transfer derived radicals can either propagate or exit the particle, leading to a number of possible events among which propagation, re-entry and termination are the most prominent. Emulsion polymerisation is a complex system based on a mechanism of a large number of interrelated kinetic and thermodynamic events.

A distribution of droplet sizes is obtained when an oil-in-water emulsion is created by the application of shear force to a heterogeneous fluid containing surfactant. The fate of the distribution is determined by the inter droplet mass transfer (Ostwald ripening) which in general terms describes the effect that larger bodies tend to grow at the expense of smaller ones through the diffusion of material. If the small droplets are not stabilised against diffusional degradation, they will eventually disappear, increasing the average droplet particle size. The disappearance of the small droplets can be very fast.[22]

The effect of the Ostwald ripening process is founded on the principle that the chemical potential of the material near an interface is higher than that of an imaginary interface-free bulk phase. The Laplace pressure gives the difference in chemical potential ($\Delta\mu$) between the droplet material (μ_d) and the bulk material (μ_b) and takes the form of equation 5.1 for spherical liquid droplets:[23]

$$\Delta\mu = \mu_d - \mu_b = \frac{2\,\sigma\,v_b}{r} \qquad 5.1$$

where σ is the surface tension of the liquid-liquid interface, v_b is the volume of a single molecule and r the radius of the droplet. In order to attain a state of lower energy (minimizing $\Delta\mu$) and considering the dependence of $\Delta\mu$ on r in equation 5.1, there will be a driving force for the migration of material from the smaller droplets to the larger droplets. As the migration of material from the smaller droplets to the larger ones continues, the smaller ones will eventually disappear, resulting in the formation of a single droplet (complete phase separation).

5.1.2 Miniemulsion

A miniemulsion polymerisation is intermediate in behaviour between a microemulsion and an ordinary macroemulsion polymerisation. There are some obvious differences between macroemulsion polymerisation and miniemulsion polymerisation. In macroemulsion polymerisation, the latex particle does not correspond to the initial emulsion droplet, and kinetic processes establish the size, where kinetic parameters, such as temperature or the amount of initiator, play a predominant role. These factors are less important in miniemulsion polymerisation, where the latexes are essentially a polymerised copy of the original pre-dispersed droplets. The size of the original droplets is essentially given by the dispersion process and droplet stability, but not by polymerisation parameters. For a macroemulsion polymerisation, the diameters of the monomer droplets are between one and 10 μm at the start of the reaction,[1] in comparison to miniemulsion monomer droplets, which are between 50 nm and 500 nm.[24] The small droplets of a miniemulsion are formed through ultra-high shear, usually by probe-sonication of the emulsion. During this preparation stage a steady state droplet size is obtained only after a certain minimum energy input.[25,26] The relative amounts of water, organic materials and surfactant determine this equilibrium droplet size. To be able to maintain such small droplets, they need to be stabilised colloidally (against coalescence by collision) and thermodynamically (against Ostwald ripening by diffusion processes). Stabilisation against coalescence is achieved by the addition of an appropriate surfactant. The small droplets will disappear if they are not stabilised against Ostwald ripening. Diffusional stabilisation of a miniemulsion polymerisation system is achieved by the addition of a small quantity of an extra very hydrophobic component (a costabiliser) to the droplet phase. These costabilisers are (normally only added in small quantities) of a highly monomer-soluble and water-insoluble agents e.g. hexadecane, dodecyl mercaptan and stearyl methacrylate. The effectiveness of these costabilisers is based on the osmotic pressure that they introduce to partly counterbalance the Laplace pressure, which then effectively minimises the driving force for inter-droplet mass transfer (Ostwald ripening). This effect is quantified in equation 5.2 through the addition of a term on the right hand side of equation 5.1:[23]

$$\Delta\mu = \mu_d - \mu_b = \frac{2\,\sigma\,v_b}{r} - \frac{\eta\,k_B\,T\,v_b}{(4\pi/3)\,r^3} \qquad 5.2$$

where η is the number of hydrophobe molecules inside a particle, k_B is Boltzmann's constant and T is the absolute temperature. The total free energy of the system is found by integration of the chemical potential over all of the material, i.e., over all droplets of all volumes. An important constraint on the minimisation of the total free energy is added by the presence of the costabiliser molecules, namely that of a constant number of droplets. If the costabilisers are very insoluble in the continuous phase and equally distributed over all of the droplets, then the droplets initially formed cannot disappear completely by monomer depletion. So, in the case where a number of large particles increase in volume at the expense of the smaller ones, then the osmotic pressure term for the small droplets rapidly becomes larger as r decreases, but because the hydrophobic molecules are present, the system cannot be relieved of the small, high energy droplets, thus increasing overall energy, and preventing the formation of large numbers of such particles. Once the costabiliser molecules can no longer be considered to be dilute, equation 5.2 is strictly speaking no longer valid. However, the formula reasonably indicates the trend in chemical potential when r decreases.

The approach to initiation of miniemulsion polymerisation is to initiate the polymerisation in each of the small, stabilised droplets, meaning that polymerisation takes place in small nanodroplets (nano bulk reactors). Micellar nucleation, droplet nucleation and homogeneous nucleation are currently discussed in literature as the three particle nucleation mechanisms for heterophase polymerisations.[1,2,27] As explained in Section 5.1.1, for a typical macroemulsion carried out above the cmc of the surfactant, the predominant mechanism for particle formation is micellar nucleation. The oligomeric radicals (generated in the water phase) enter micelles and continue growing, attracting monomer from the monomer droplets. So, for this mechanism, the reaction ingredients (e.g. monomer) must migrate from the droplets, through the water phase, into the growing particles, which were formed by the conversion of the micelles into the polymer particles. In miniemulsion polymerisation micellar nucleation is very unlikely. The reason for this is that the surface tensions of miniemulsions are usually well above those of saturated surfactant solutions, i.e. there are no micelles present.

So, in the case of miniemulsion polymerisation, the absence of micelles and the increased surface area of the droplet phase (smaller droplets have a much larger interfacial area with the continuous phase) promote droplet nucleation. The oligomeric radicals that are formed in the water phase enter the monomer droplets and start polymerisation in the droplets. For this mechanism, it is not necessary for the monomer to diffuse through the water phase, as the monomer droplets themselves are converted into polymer particles. So, in the ideal miniemulsion system, droplet nucleation is the preferred mechanism, where every droplet is nucleated and the particle number does not change during polymerisation (Scheme 5.2).

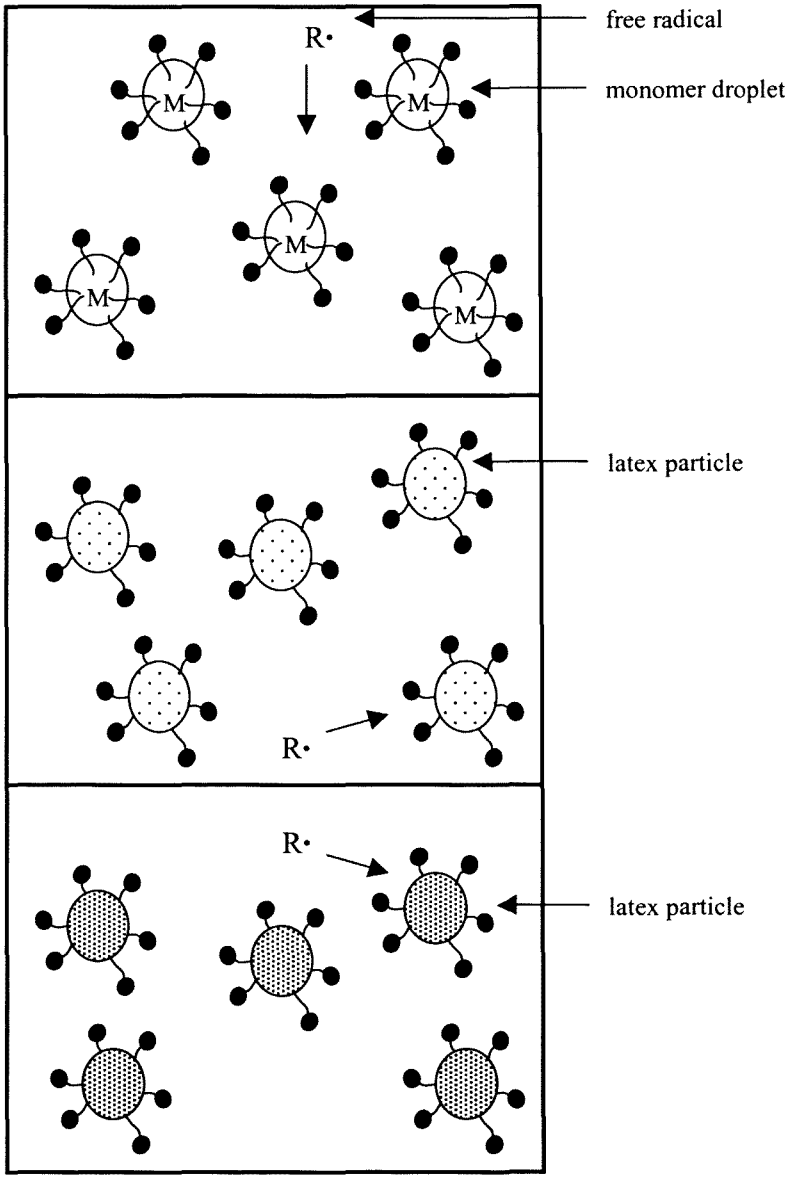
The third mechanism, homogeneous nucleation, is important when the amount of surfactant added is below the cmc and in surfactant-free emulsion polymerisation systems, but also forms new particles in miniemulsion polymerisation.[28,29] This particle formation mechanism takes place when an oligomeric radical (z-mer) in the water phase does not enter a droplet or micelle, but propagates, until it reaches a critical chain length (j_{crit}) upon which it is no longer soluble in the aqueous phase and collapses to form a proto-particle. The relative amount of particles formed through homogeneous nucleation depends on the rate of formation of a j_{crit}-mer compared with the reaction lifetime. This rate depends on the $k_{p_{aq}}$ (the rate coefficient for propagation in the aqueous phase) of the monomers used, the solubility of these oligomers in the aqueous phase and the rate of loss of the oligomeric species through termination, droplet/particle/micellar entry. The precipitated oligomeric radicals form primary particles that adsorb surfactant molecules, bringing about their stabilisation, and absorb monomer, allowing further propagation and growth. The type of initiator used, the number of droplets, the amount of monomer in the water phase and the propagation rate constant in the water phase are all important factors that determine the extent of homogeneous particle nucleation. The overall picture is quite complex and this model has become known as the HUFT (Hansen-Ugelstad-Fitch-Tsai) theory.[30] It has also been well explained by Gilbert.[1]

The presence of additional nucleation mechanisms, besides droplet nucleation, and the probability that not all of the monomer droplets are converted into polymer particles are factors that cause experimental miniemulsion systems to deviate from the ideal situation

described earlier. Although all of the droplets share the same osmotic pressure because of the addition of a costabiliser, the difference in osmotic pressure among the droplets will increase during the course of the reaction if some of the droplets are nucleated and others are not. Those droplets that have not been nucleated and do not contain polymer will eventually become monomer reservoirs capable of supplying monomer to the reacting polymer particles.

Macroemulsion and miniemulsion systems should in principle provide an environment with ideal conditions for conducting living radical polymerisation (e.g. RAFT). In the case of both systems, irreversible radical-radical termination is minimised through compartmentalisation, which allows higher polymerisation rates compared to bulk or solution systems. The continuous aqueous phase provides a good medium to remove the heat of reaction, and the polymer dispersion has a relatively low viscosity and is thus easy to handle. The advantage of a miniemulsion system over that of a macroemulsion system is the absence of complex particle formation and mass transfer events. In a miniemulsion reaction, each of the monomer droplets are considered as miniature bulk reactors, completely segregated from the other droplets. It has been shown by many research groups that the bulk environment is suitable for conducting living radical polymerisation.[20,31,32]

Scheme 5.2: A schematic representation of the progress of a miniemulsion polymerisation.



This means that in the case of a miniemulsion system each of the droplets can be considered as a small bulk reactor independent of the other droplets. As mentioned earlier there are several factors that cause experimental miniemulsion systems to deviate from the proposed ideal system previously described. If only a small part of the original population of droplets is nucleated, then the remaining unnucleated droplets will serve as reservoirs for the reacting particles, and the monomer and RAFT agent (within the reservoirs) will be transported through the aqueous phase. This eliminates one of the

main advantages of miniemulsion polymerisation, which is to restrict mass transfer events. A major effect will be that the RAFT agent may be arriving later at the polymerisation site, which will cause a broadening of the molar mass distribution because the new chains start growing later in the polymerisation.

If secondary nucleation (the most likely sources of this being micellar entry and homogeneous nucleation) takes place it will lead to the formation of particles, which do not contain any RAFT agent, since all of the transfer active moiety is attached to polymer chains in the first generation of droplets/particles. This means that in these particles, uncontrolled polymerisation will take place, which will broaden the overall molar mass distribution.

5.2 Experimental

5.2.1 Reagents

Methyl methacrylate (MMA, 98%) and methacrylic acid (MAA, 98%) were obtained from the Plascon Research Centre, University of Stellenbosch. The MMA was washed with a 0.3 M solution of KOH and then distilled under vacuum to remove the inhibitor. The MAA was distilled under vacuum. 2,2-Azobis(isobutyronitrile) (AIBN, Delta Scientific, 98%) was recrystallised twice from methanol. Potassium persulfate (KPS, Acros, 99 %), the nonylphenyl surfactants containing 5 ethylene oxide units (Aldrich, 99 %) and hexadecane (HD, Aldrich, 99 %) were all used as received. The surfactant used was the sodium salt of nonylphenoxypolyethyleneoxyethanol sulfate (Polystep B-27, Stepan Company). Polystep B-27 is an aqueous solution (31% actives) of a nonyl phenol ethoxylate sulfate containing approximately 4 moles of ethylene oxide per surfactant molecule. 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid was prepared according to the method described in Section 4.2.4. The synthesis and characterisation of hydrophobic macromonomer one (HM1, 99% yield, purity (^{1}H NMR) > 97 %) is described in Section 4.2.3.

5.2.2 Sample preparation and characterisation

5.2.2.1 Size exclusion chromatography:

The molar masses and molar mass distributions of the polymers were measured by size exclusion chromatography (SEC). The chromatograph used was a Waters 600E module with a Waters 410 differential refractometer. THF was used as mobile phase with a flow rate of 1.0 mL min^{-1} at a column temperature of 35 °C. Four Phenogel columns (300mm × 7.80mm) with respective pore sizes of 100, 10^3, 10^4 and 10^5 Å were used in series. The system was calibrated using six narrow molar mass PMMA standards (Pressure Chemicals), in the range of 2 500 – 900 000 g mol^{-1}. Molar masses are reported as PMMA equivalents. Prior to SEC analysis, methacrylic acid groups were converted to methyl methacrylate units with tetramethylammonium hydroxide and methyl iodide in THF at 80 °C.[33] Samples were prepared for SEC analysis by drying the polymer *in vacuo* and redissolving *ca.* 5 mg of the polymer in 1 mL THF.

5.2.2.2 *Rheology:*

The rheological analyses of the various samples were done with a Paar Physica MCR 300 rheometer, using a cone (50 mm, 1° angle) and plate (50 mm) measuring system. All rheological measurements were conducted at 25 °C.

Latex rheology: The rheological behaviour of the polymers was tested in a well-characterised core-shell emulsion. The details of the core-shell emulsion are given in Section 3.2.2. The rheology samples were made up of 20 g of the core-shell emulsion, 2.5 g (0.4 g active compound) of the rheology modifier made from the miniemulsion reaction described below, and 7.5 g of water. The rheology samples were prepared by mixing the core-shell emulsion, the miniemulsion (rheology modifier) and water after which the pH of the mixture was adjusted to 9 using 2-amino-2-methyl-1-propanol (AMP 95, 95% by weight + 5% water).

Solution rheology: 7.5% and 15% aqueous solutions, at pH 9, were prepared for the different rheology modifiers synthesised. AMP 95 was used to neutralise the polymer solutions. The pH was adjusted to 9 by the addition of AMP 95.

5.2.2.3 *Light scattering:*

Particle diameters were determined by light scattering on a Malvern Zetasizer 1000 HSa. For this purpose, samples were diluted with 1 mM NaCl solution.

5.2.2.4 Transmission electron microscopy:

For transmission electron microscopy (TEM) analysis, 2 mL of the latex was added to an excess of MeOH to aid precipitation of the particles. The solution was homogenised by shaking and transferred to a copper TEM grid by pipette. The grid was left to dry at ambient temperature before it was stained with uranyl acetate. Analyses were done on a JEM - 200CX (JEOL Ltd., Tokyo, Japan) TEM.

5.2.3 Miniemulsion polymerisation procedure

All of the miniemulsions reactions were prepared and carried out according to the following procedure. The MMA, MAA, and HM 1 (if used) were first mixed with hexadecane, the RAFT agent (4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid, if used), and AIBN (if used). This organic phase was then added to the aqueous phase (water, polystep B27), under vigorous stirring. After 60 min, the mixture was ultrasonified, using a Sonics & Materials Inc. Vibracell VCX 75 ultrasonicator, for a period of 5 min at 95% amplitude (50.2 kJ = total energy output during that period). The obtained stable miniemulsion was then transferred to a conventional 250 mL reactor, equipped with a condenser, a thermocouple, and a nitrogen inlet. The reactor contents were purged with UHP grade nitrogen gas for 30 min to remove oxygen from the reaction mixture. For the reactions where KPS was used as initiator, the reactor, containing the reaction mixture, was immersed in a thermostatted oil bath while the temperature was raised to 80 °C. Finally, the addition of KPS dissolved in 5 mL of water started the polymerisation reaction (time zero).

In the reactions where AIBN was used as initiator, the thermostatted oil bath was first preheated to 80 °C and then the reactor, containing the reaction mixture, was immersed in the oil bath. Zero time for the polymerisation reaction was (arbitrarily) set when the reaction mixture in the reactor reached 65 °C. The conversion of monomer as a function of time and the evolution of molar masses and molar mass distribution as a function of

monomer conversion was followed by the regular withdrawal of samples. Tables 5.1 and 5.2 contain the experimental conditions for all of the miniemulsion polymerisations performed for this study.

Table 5.1: General recipe for the RAFT miniemulsion polymerisations at 80 °C.

Ingredient	Concentration
Organic Phase	
monomer (MMA/MAA)	20 % final solids content
RAFT agent	(0.001 – 0.00394) mol
Hexadecane	0.4 g
Water Phase	
distilled and deionised water	100 mL
polystep B27	1 g
initiator	0.000055 mol

Table 5.2: Summary of experimental conditions of all miniemulsion polymerisations carried out in this study. All of the reactions were carried out at 80 °C, using 0.000055 mol of initiator (AIBN or KPS).

experiment	MMA (mol)	MAA (mol)	HM 1 (mol)	RAFT (mol)
1	0.10	0.10	-	0.000394
2	0.10	0.10	-	0.000197
3	0.10	0.10	-	0.0001
4*	0.10	0.10	-	0.000394
5*	0.10	0.10	-	0.000197
6*	0.10	0.10	-	0.0001
7	0.15	0.05	-	0.000394
8	0.15	0.05	-	0.000197
9	0.15	0.05	-	0.0001
10	0.18	0.02	-	0.000394
11	0.18	0.02	-	0.000197
12	0.18	0.02	-	0.0001
13	0.20	-	-	0.000394
14	0.20	-	-	0.000197
15	0.20	-	-	0.0001
16	0.10	0.10	-	-
17*	0.10	0.10	-	-
18	0.0995	0.0995	0.001	0.00394
19	0.09875	0.09875	0.0025	0.00394
20	0.0975	0.0975	0.005	0.00394

* Reactions initiated with KPS

Table 5.3: Summary of experimental results of all the miniemulsion polymerisations carried out in this study. Particle diameters were determined by light scattering on a Malvern Zetasizer 1000 HSa.

Experiment	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Number average particle diameter (nm)	Polydispersity
1	39480	1.33	50	0.09
2	71530	1.35	46	0.11
3	145945	1.49	60	0.10
4	26410	1.70	65	0.12
5	60500	1.50	72	0.09
6	135000	1.65	80	0.11
7	29610	1.27	78	0.08
8	67200	1.41	83	0.09
9	128570	1.40	62	0.09
10	31430	135	30	0.11
11	78290	1.58	32	0.10
12	127450	1.75	30	0.12
13	39570	1.27	162	0.09
14	58740	1.36	138	0.09
15	134790	1.56	105	0.11
16	487330	2.34	29	0.08
17	535450	2.55	33	0.09
18	45590	1.41	180	0.12
19	46300	1.51	210	0.11
20	54180	1.52	198	0.13

5.3 Results and discussion

5.3.1 Polymerisation reactions

The results of several experimental runs will be discussed to illustrate the use of RAFT polymerisation in miniemulsion in order to synthesise model alkali-soluble rheology modifiers. Special attention will be given to considering the effects of using an oil-soluble (AIBN) and a water-soluble (KPS) initiator and changing the ratio of MMA:MAA. None of these miniemulsion polymerisation reactions showed any colloidal instability of the latexes, and the final latex products were stable for a period of at least several months.

In this case where a water-soluble monomer (MAA) is copolymerised with MMA, a mixed mode of particle nucleation (i.e. monomer droplet nucleation, homogenous nucleation and micellar nucleation) might be expected. Although this scenario is probable, the good control over the molar mass and molar mass distribution of the polymers synthesised (to be described in the next section) indicates that monomer droplet nucleation was probably the predominant mechanism. Micellar nucleation is unlikely because of the low surfactant concentration (below the cmc) that is used in the miniemulsion reactions. As mentioned in Section 5.1.2, particles formed by either micellar nucleation or homogeneous nucleation will undergo uncontrolled free radical polymerisation, because there is expected to be no RAFT agent present in these particles. Chern *et al.*[34] showed that the incorporation of a small amount of acrylic acid (AA) into the miniemulsion polymerisation of styrene (sodium dodecyl sulfate/stearyl methacrylate stabilised polymerisation) promotes monomer droplet nucleation. This was ascribed to the enhanced water phase polymerisation because of the water-soluble AA, which should favour the formation of particle nuclei in the water. They postulated that the composition of the oligomeric radicals generated in the water phase is rich in AA. The critical chain length for the AA containing radicals to precipitate out of the aqueous phase should be longer compared with oligomeric radicals obtained from the polymerisation in the absence of AA. The probability of the relatively hydrophilic radicals being captured by the monomer droplets (exhibiting a very large droplet surface area) increases. As a result

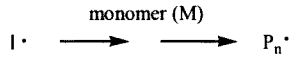
more monomer droplets can be nucleated upon collision with these radicals induced by shear force.

Figures 5.1 (a) and Figure 5.2 (a) show conversion-time profiles for several miniemulsion polymerisations. When the rate of polymerisation of the experiment in the absence of a RAFT agent (experiment 16 in Figure 5.1 (a) and experiment 17 in Figure 5.2 (a)) is compared with that of the same experiments with a RAFT agent (experiments 1 – 3 in Figure 5.1 (a) and experiments 4 – 6 in Figure 5.2 (a)), it is seen that the addition of the RAFT agent to the system causes a large decrease in the rate of polymerisation. As mentioned by Butté *et al.*,[35] it seems reasonable to assign this decrease in the polymerisation rate to the exit of the radical formed after fragmentation of intermediate species **2** (Scheme 5.3) in the particles. It is conceivable that the short radical R•, released when the RAFT agent underwent the first transfer reaction, escapes from the particle to the water phase.[36] It is very likely that the exited radical will terminate, either upon re-entry into a particle already containing a growing radical, or in the water phase with initiator derived radicals. The result of this is that one or two of the particles lose their propagating radical per exit event; these must then be nucleated again to become sites for polymerisation. This loss process is probably only important early in the reaction, since this will be the only time when there is little polymer in such particles, and the number of short radicals capable of exit is at a maximum. Lower particle numbers could also result from nucleation being less efficient in a RAFT containing miniemulsion than in a conventional miniemulsion polymerisation system. This was observed by Lansalot *et al.*, who showed that the rate of polymerisation is roughly proportional to the number of particles.[31]

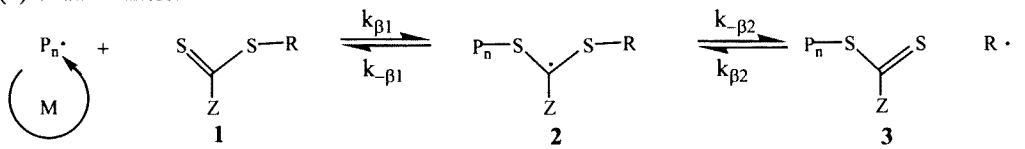
Figures 5.1 (a) and 5.2 (a) show that the polymerisation rate increases as the amount of RAFT agent is decreased. Lansalot *et al.* also attributed this behaviour to exit and entry events. Thus, the polymerisation rate decreases because nucleation efficiency decreases (leading to a decrease in the number of particles containing radicals) as a result of the exit of the R• radical generated by the addition of an entering radical to the RAFT agent. The probability of these events taking place increases as the initial amount of RAFT agent increases.

Scheme 5.3: Schematic representation of the RAFT mechanism.

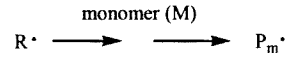
(a) Initiation



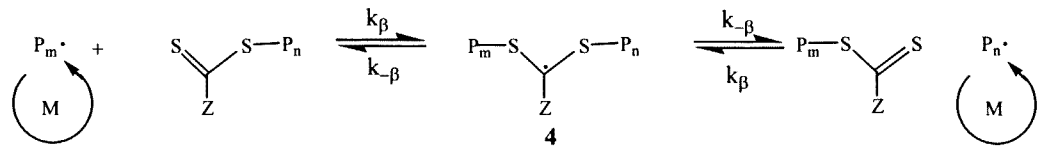
(1) Chain Transfer



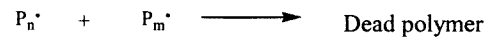
(2) Reinitiation



(3) Chain equilibration



(b) Termination



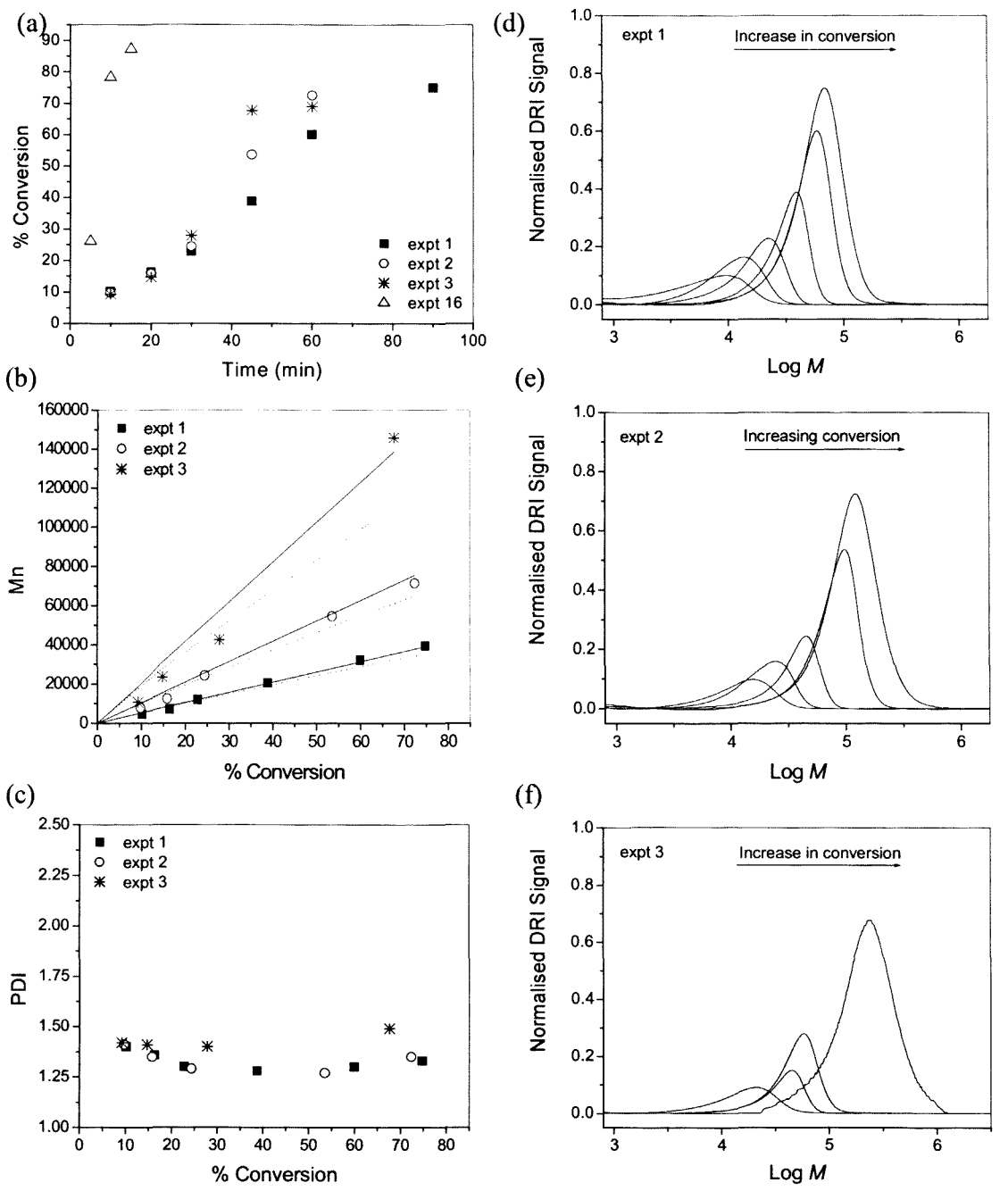


Figure 5.1: 50:50 MMA:MAA, AIBN initiator (a) Evolution of monomer conversion as a function of reaction time, (b) evolution of number-average molar mass (straight line: theoretical number-average molar mass predicted by equation 3.1; dotted line: theoretical number-average molar mass predicted by equation 3.2.), (c) the PDI, as functions of monomer conversion, for reactions 1 – 3, using AIBN as initiator at 80 °C. (d) – (f) Evolution of molar mass distributions with conversion for experiments 1 – 3, respectively. See Table 5.1 and Table 5.2 for detailed experimental conditions. Evolution of monomer conversion as a function of reaction time for reaction 16 is also given in Figure 5.1 (a).

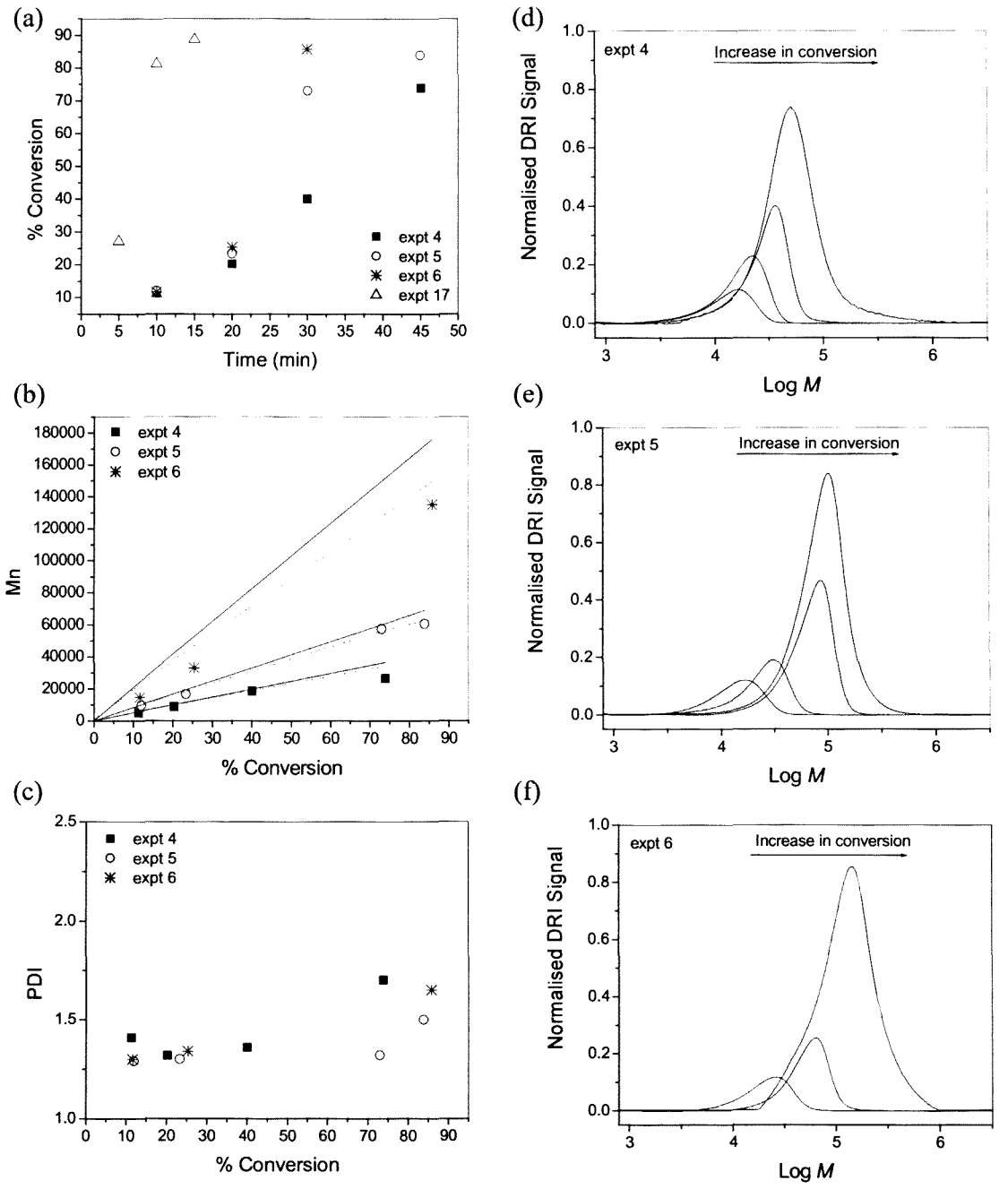


Figure 5.2: 50:50 MMA:MAA, KPS initiator (a) Evolution of monomer conversion as a function of reaction time, (b) evolution of number-average molar mass (straight line: theoretical number-average molar mass predicted by equation 3.1; dotted line: theoretical number-average molar mass predicted by equation 3.2.), (c) the PDI, as functions of monomer conversion, for reactions 4 – 6, using KPS as initiator at 80 °C. (d) – (f) Evolution of molar mass distributions with conversion for experiments 4 – 6, respectively. See Table 5.1 and Table 5.2 for detailed experimental conditions. Evolution of monomer conversion as a function of reaction time for reaction 17 is also given in Figure 5.2 (a).

5.3.1.1 Type of initiator

For miniemulsion polymerisation, the initiator can be either oil-soluble or water-soluble. In the case of an oil-soluble initiator, the initiator was dissolved in the organic phase prior to emulsification. For miniemulsions (using an oil-soluble initiator), the reaction can start either from radical activity within the oil-phase[37] or through radical activity due to entry from the aqueous-phase.[38] In the case of a water-soluble initiator, the polymerisation proceeds by entry of radicals from the water phase, and are similar to conventional emulsion polymerisation with such initiators. The use of oil-soluble initiators in miniemulsion reactions is preferred for monomers with high water solubility (e.g. MMA), in order to prevent secondary particle nucleation in the water phase, or those with extremely low water solubility (e.g. lauryl methacrylate), where the monomer concentration in the water phase is not high enough to create oligomeric radicals capable of entering the droplets. The k_d values for AIBN and KPS at 80 °C are $1.4 * 10^{-4}$ s^{-1} and $8.6 * 10^{-5}$ s^{-1}, respectively.

In Figure 5.3, the conversion-time profiles of the AIBN initiated reactions 1 – 3 are compared to those of the KPS initiated reactions 4 – 6. Figure 5.3 also contains the conversion-time profiles for reactions 16 (AIBN) and 17 (KPS) containing no RAFT agent. A significant difference in the polymerisation rates can be seen for the RAFT containing reactions. For reactions containing the same amount of RAFT agent the polymerisation rate for KPS initiated reactions is almost twice as fast as comparable AIBN initiated reactions. A possible explanation for this is that additional particles are generated (homogeneous nucleation), leading to an increase in the polymerisation rate (given the same average number of propagating radicals per particle). These newly formed particles would be deficient in RAFT agent, resulting in uncontrolled polymerisation. There is no evidence for such a process found in the molar mass distributions for the AIBN initiated reactions (Figures 5.1). For both the AIBN and KPS initiated systems there is a tail towards the low molar mass side, which indicates that some termination that has taken place throughout the course of the reaction. However, for the KPS initiated systems (Figure 5.2), there is a tail to high molar mass at high conversions, which indicates some uncontrolled polymerisation, and possibly extensive termination late in the reaction, taking place. This is probably due to diffusion control of

the addition step causing a loss of control. There are two factors that show that very little chain growth is taking place in the absence of a RAFT agent. There is no high molar mass distribution of chains formed early in the reaction. The molar mass of the uncontrolled polymer chains would be expected not to change with time, and their molar mass would be significantly different from the growing component. The difference in the polymerisation rates of the uncontrolled reactions 16 (AIBN) and 17 (KPS) is not as big as is the case with the RAFT containing reactions. Reactions 16 and 17 also show very similar particle size and number average molar mass (Table 5.3).

Other factors that determine the rate of reaction are the average number of propagating radicals per particle ($\bar{n}$). In the case of a 0-1 system $\bar{n}$ depends on the relative rates of entry (or generation of radicals that are not terminated in the particle) and exit (termination is not rate determining in these systems). It is very likely that the rate of entry is much higher in the KPS system, since there is much more initiator in the aqueous phase. Thus, for a 0-1 system, $\bar{n}$, and the resulting rate of reaction, will be significantly increased in the case of the KPS initiated system. However, the current system could very well be pseudo-bulk, in which case $\bar{n}$ depends on the relative rates of initiation/entry and termination/exit. Again, the rate of radical production (initiation/entry) will be much higher for the KPS initiated system, for the same reasons mentioned earlier.

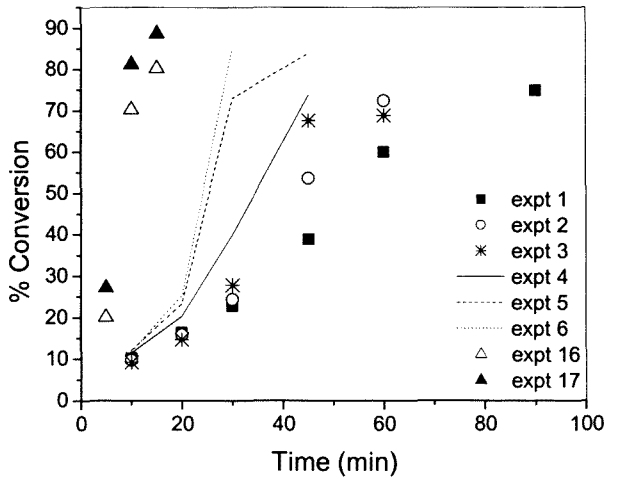


Figure 5.3: Evolution of monomer conversion as a function of reaction time for reactions 1 – 3 (AIBN initiated), reactions 4 – 6 (KPS initiated) and reactions 16 (AIBN) and 17 (KPS) containing no RAFT agent.

Although AIBN is a primarily oil-soluble initiator, it shows a significant production of free radicals in the water phase, and emulsion reactions with AIBN as initiator show similar polymerisation kinetics to those polymerisations employing water-soluble initiators.[39,40] One trend of thought is that if the oil-soluble initiator decomposes in the micelle or particle (both assumed to be quite small in size), the two newly formed free radicals will undergo bimolecular termination with each other before any other events such as monomer propagation or free radical exit can occur. So, in this case, the origin of the free radicals that initiate polymerisation arises from the decomposition of the small amount of initiator dissolved in the water phase.[41-43] Contrary to this, some researchers assume that one of the newly born free radicals has enough time to desorb from the micelle or particle before mutual termination takes place.[37,39,40,44,45] The remaining free radical is then free to propagate. Luo *et al.*[38] concluded that the free radicals originating in the particle phase contribute to the rate of polymerisation and that this contribution increases with increasing particle size; in the case of polymer particles with diameters up to approximately 100 nm, polymerisation is initiated from free radicals originating in the water phase.

Since the final polymer particles, for most of the reactions, are smaller than 100 nm (diameter), one can assume that the monomer droplets are smaller than 100 nm and therefore initiation of polymerisation is mainly from radicals derived in the water phase. The final polymer particles from reactions 13–15, containing only MMA, are larger than 100 nm and these reactions are expected to be a pseudo-bulk system.[1] Particle size data (light scattering) are presented in Table 5.3 for each of the miniemulsion reactions, and two TEM images, for reaction 3, are shown in Figure 5.4. From the TEM images there appears to be a range of particle sizes and this could be due to differences in nucleation times. The concentration of free radicals in the water phase for KPS initiated reactions would be significantly higher than in the reactions where AIBN is used as initiator. A higher concentration of free radicals leads to a higher polymerisation rate,[31], which explains the higher polymerisation rates observed for the KPS, initiated miniemulsion systems.

For each of the three reactions in Figures 5.1 (b) and 5.2 (b), the amount of initiator is kept constant while the amount of RAFT agent is decreased, in order to obtain higher molar mass polymers. For reactions 1 – 3 in Figure 5.1 (b), the experimental number average molar mass data compares well with the calculated theoretical values from equations 3.1 and 3.2. In the case of reaction 3, there is an increase in the molar mass and polydispersity towards the end of the reaction (as high conversion is reached). At high conversion the high chain length and viscosity in the particles will probably lead to the addition step of the RAFT process becoming diffusion controlled, leading to an increase in the free radical concentration, increased termination rates, and lack of control of chain growth. During this period, there would be a broadening to the high molar mass end, which is observed.

In the curve describing the evolution of the experimental number-average molar mass for the KPS reactions 4 – 6 (Figure 5.2 (b)), one can clearly see how the experimental results curve away (towards lower molar mass) from the calculated theoretical values at higher conversion. It is expected that the rate of reaction will drop for at least two reasons: loss of initiator and increased termination rates towards the end of the reaction. The termination rates increase due to less propagation per unit time (monomer depletion) and the possible loss of control when the addition step, of the RAFT process, becomes diffusion controlled. This also explains the broadening of the molar mass distribution towards the end of the reactions, as can be seen in Figure 5.2 (c).

(a)

(b)

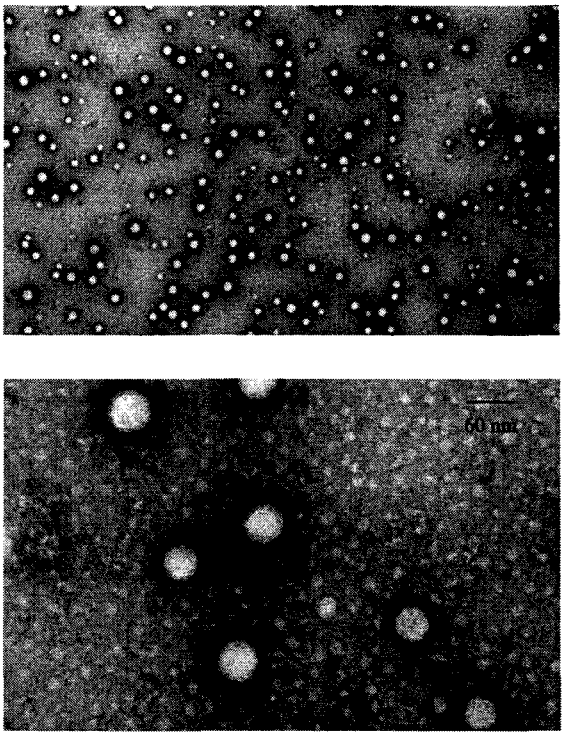


Figure 5.4: TEM images of polymerised miniemulsion 3. (a) 10 000 magnification (b) 50 000 magnification.

5.3.1.2 Changing the ratio of MMA:MAA

If one compares the conversion-time profiles of the various reactions containing the same amount of RAFT agent, it is clear that the polymerisation rate decreases as the ratio of MMA:MAA increases. Figure 5.5 shows the evolution of monomer conversion as a function of reaction time for reactions 1, 7, 10 and 13. For all of these reactions, the [RAFT], [I] and reaction conditions are constant. The only variation is the percentage of MAA in the total amount of monomer available for the reactions, which decreases from 50 % (experiment 1) to 25 % (experiment 7) to 10 % (experiment 10) to 0 % (experiment 13).

The main reason for the decrease in the polymerisation rate is because the propagation rate constant (k_p) for MAA[46] is higher than that of MMA.[47,48] Thus, the reactions containing a higher percentage of MAA in the total amount of monomer available for the

reaction, will have a higher average k_p. A higher average k_p will lead to a higher polymerisation rate for the specific reaction.

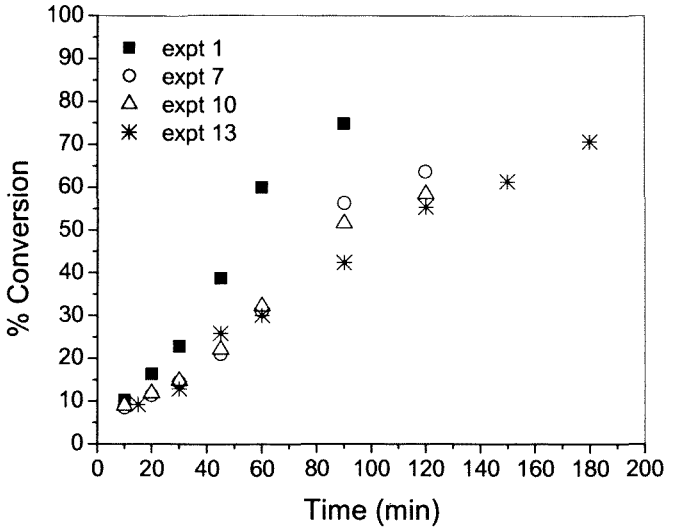


Figure 5.5: Evolution of monomer conversion as a function of reaction time for reactions 1 (50 % MAA), 7 (25 % MAA), 10 (10 % MAA) and 13 (0 % MAA). RAFT concentration was the same for all the reactions.

Reactions 1 – 3 in Figure 5.1 have a monomer ratio of 50:50 (MMA:MAA), reactions 7 – 9 in Figure 5.6 have a monomer ratio of 75:25 (MMA:MAA), reactions 10 – 12 in Figure 5.7 have a monomer ratio of 90:10 (MMA:MAA), and reactions 13 – 15 in Figure 5.8 consist only of MMA. It is important to note that for each of the series of reactions (Figures 5.1, 5.6, 5.7 and 5.8) there was a significant decrease in the polymerisation rate as the RAFT concentration increased. The probable reasons for this were explained in Section 5.3.1.

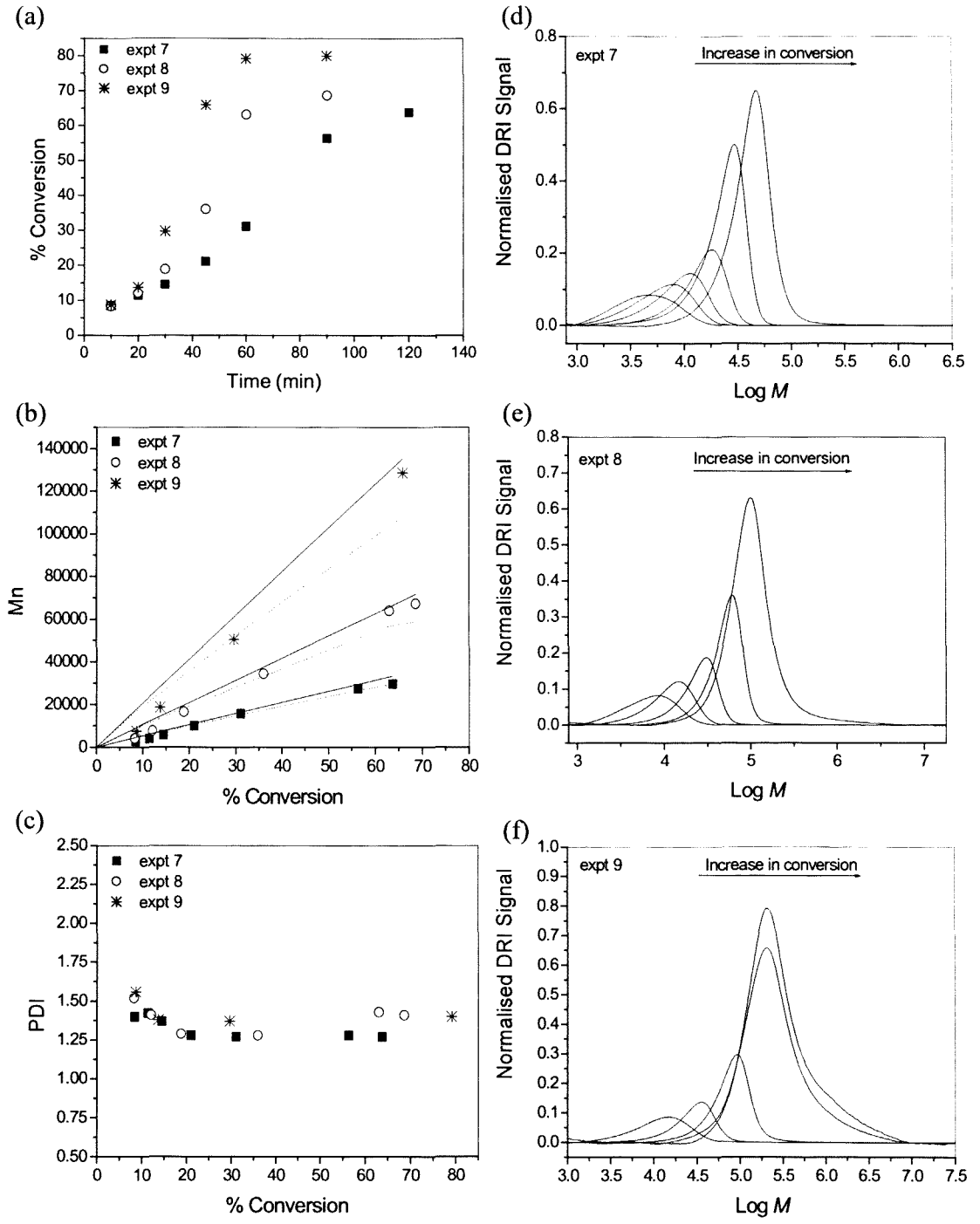


Figure 5.6: 75:25 MMA:MAA, AIBN initiator (a) Evolution of monomer conversion as a function of reaction time, (b) evolution of number-average molar mass (straight line: theoretical number-average molar mass predicted by equation 3.1; dotted line: theoretical number-average molar mass predicted by equation 3.2.), (c) the PDI, as functions of monomer conversion, for reactions 7 – 9, using AIBN as initiator at 80 °C. (d) – (f) Evolution of molar mass distributions with conversion for experiments 7 – 9, respectively. See Table 5.1 and Table 5.2 for detailed experimental conditions.

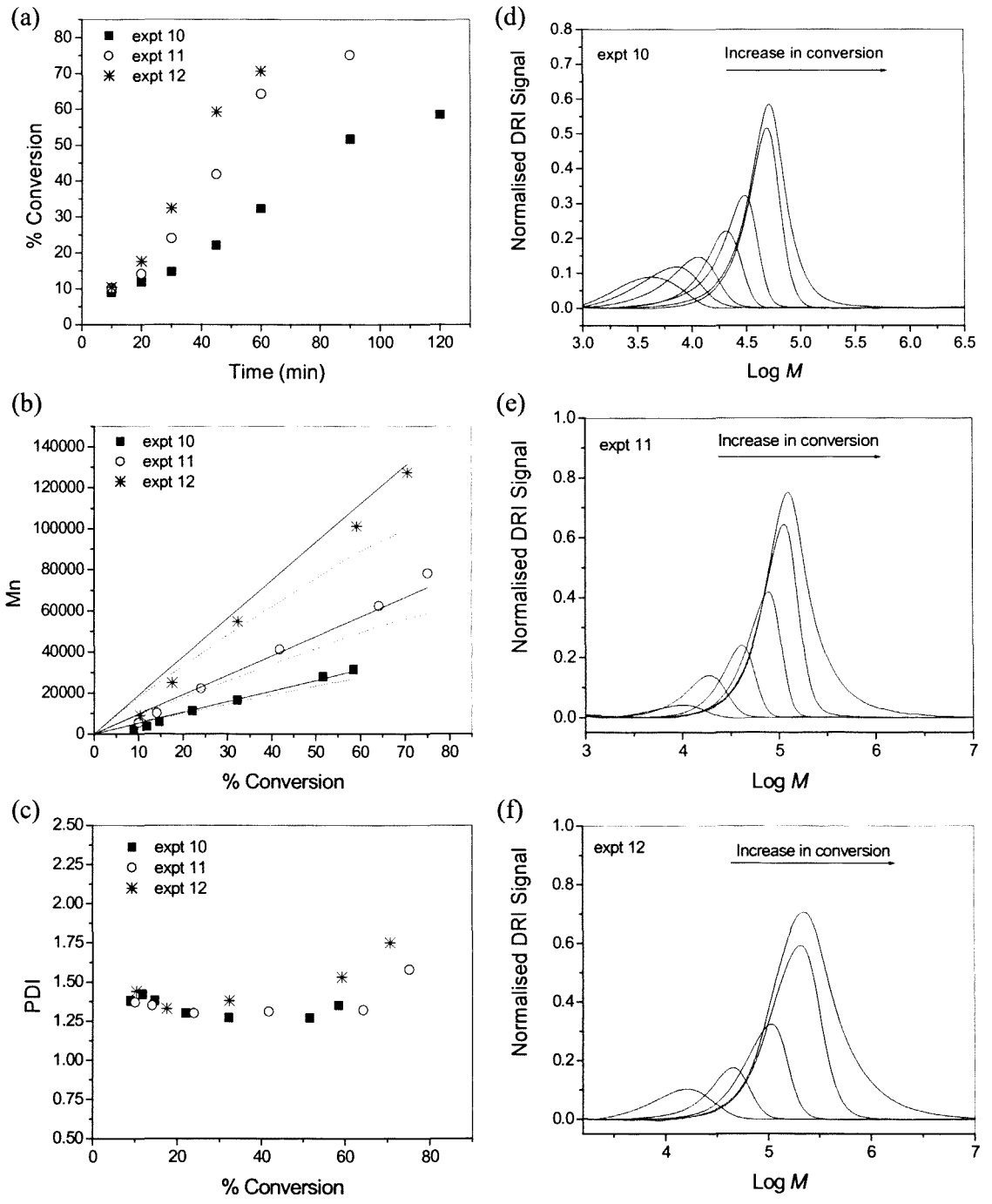


Figure 5.7: 90:10 MMA:MAA, AIBN initiator (a) Evolution of monomer conversion as a function of reaction time, (b) evolution of number-average molar mass (straight line: theoretical number-average molar mass predicted by equation 3.1; dotted line: theoretical number-average molar mass predicted by equation 3.2.), (c) the PDI, as functions of monomer conversion, for reactions 10 – 12, using AIBN as initiator at 80 °C. (d) – (f) Evolution of molar mass distributions with conversion for experiments 10 – 12, respectively. See Table 5.1 and Table 5.2 for detailed experimental conditions.

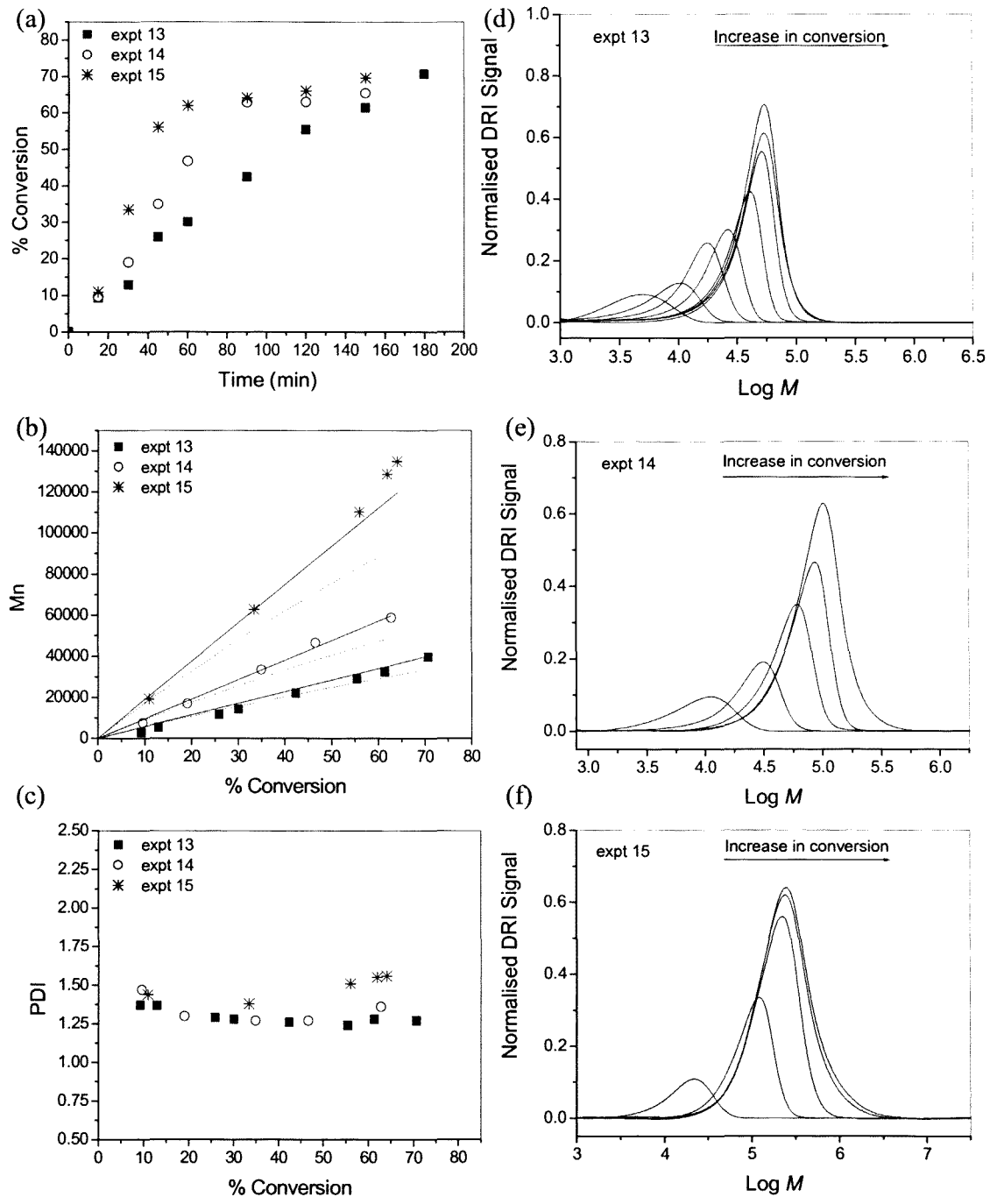


Figure 5.8: MMA, AIBN initiator (a) Evolution of monomer conversion as a function of reaction time, (b) evolution of number-average molar mass (straight line: theoretical number-average molar mass predicted by equation 3.1; dotted line: theoretical number-average molar mass predicted by equation 3.2.), (c) the PDI, as functions of monomer conversion, for reactions 13 – 15, using AIBN as initiator at 80 °C. (d) – (f) Evolution of molar mass distributions with conversion for experiments 13 – 15, respectively. See Table 5.1 and Table 5.2 for detailed experimental conditions.

Once again, equations 3.1 and 3.2 can be used to predict the evolution of the number-average molar mass with conversion. For all of the reactions in Figures 5.1 (b), 5.6 (b), 5.7 (b), and 5.8 (b), the experimental number-average molar mass is best represented by the theoretical data calculated from equation 3.1, which neglects the contribution of initiator-derived chains to the total number of chains. Although the experimental data is better fitted to the theoretical data from equation 3.1, there is not much difference between the two predictions when the RAFT/AIBN ratio is high as is the case for reactions 1 (Figure 5.1 (b)), 7 (Figure 5.5 (b)), 10 (Figure 5.6 (b)), and 12 (Figure 5.7 (b)). The probable reason for the initiator not having as large an influence on the number-average molar mass is because of the low concentration of AIBN in the water phase and the fast reaction rates, which mean little initiator decomposition will have occurred in this time. As explained earlier, for polymer particles with diameters up to 100 nm, polymerisation is mainly expected to be initiated from free radicals originating in the water phase.

Overall, the polydispersities of the polymers were in the region of 1.3 – 1.5, with some higher values (1.7) observed for the reactions where the ratio of RAFT agent/initiator is smaller. Likely causes for the broadening of the molar mass distribution are termination, inefficient transfer and a large fraction of chains being initiated throughout the course of the reaction.

5.3.1.3 Alkali-soluble polymers containing hydrophobic macromonomers

Attempts at incorporating hydrophobic macromonomers HM2, HM3 and HM4 used in Chapter 4 were not successful. After about 30 min into the reaction a definite phase separation started to appear, and after 45 min there was complete phase separation as red polymer coagulum was visible at the bottom of the reaction mixture. The reaction mixture then consisted of a white top layer (water, surfactant and remaining monomer) and a red polymer layer at the bottom of the reaction vessel. The addition of the macromonomer to the growing chains destabilises the latex particles, and phase separation occurs. The destabilisation of the latex particles is probably due to surface

activity bringing the ethylene oxide spacer units in the macromonomers towards the surface of the particles.

Incorporation of macromonomer HM1 into the alkali-soluble polymers was however successful. HM1 contains only 5 ethylene oxide spacer units between the terminal hydrophobe and the ethylenic unsaturation and is therefore less water-soluble than the other three hydrophobic macromonomers. Three associative rheology modifiers were synthesised, containing 1%, 2.5% and 5% of HM1, respectively. All three of the miniemulsion reactions were colloidally stable, and showed no coagulum formation. Tables 5.1 and 5.2 show the experimental details for the three reactions. Table 5.4 contains the molar mass and molar mass distribution results for the three associative rheology modifiers synthesised by RAFT in miniemulsion.

Table 5.4: The monomer ratios and SEC results for the polymerisation of three associative rheology modifiers by RAFT in miniemulsion containing various amounts of HM1. Tables 5.1 and 5.2 give the experimental details for the three reactions.

experiment	Composition	Monomer ratio	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
18	MMA/MAA/HM1	49.5/49.5/1	45590	1.41
19	MMA/MAA/HM1	48.75/48.75/2.5	46300	1.51
20	MMA/MAA/HM1	47.5/47.5/5	54180	1.52

5.3.2 Rheology

The polymers synthesised in reactions 1 – 20 will be referred to as rheology modifiers (RM) 1 – 20, respectively. Table 5.3 gives a summary of the experimental results (molar mass, molar mass distribution and number average particle diameter) for RMs 1 – 20.

5.3.2.1 Steady shear viscosity of the conventional rheology modifiers

Figure 5.9 shows the steady shear viscosity of the latex solutions thickened with conventional RMs 1 – 3. The initial monomer ratio of MMA:MAA, for experiments 1 – 3, was 50:50. Similarly to the results obtained in Section 3.3.2.1 for the rheology

modifiers synthesised in solution, each of the rheology profiles shows a significant decrease in viscosity at a critical shear stress (yield stress). An increase in the molar mass, results in an increase in the viscosity and the yield stress. The increase in the viscosity and yield stress is due to the higher molar mass polymer chains, which lead to a higher degree of chain entanglement. This is typical behaviour of conventional aqueous rheology modifiers that only thicken the aqueous phase by hydrodynamic volume and molecular chain entanglement.[49] The hydrodynamic thickening mechanism of conventional alkali-soluble rheology modifiers, described in Section 2.3.5.2, and the conceptual model proposed in Section 3.3.2.1 are also applicable to the behaviour of the conventional rheology modifiers shown in Figure 5.9.

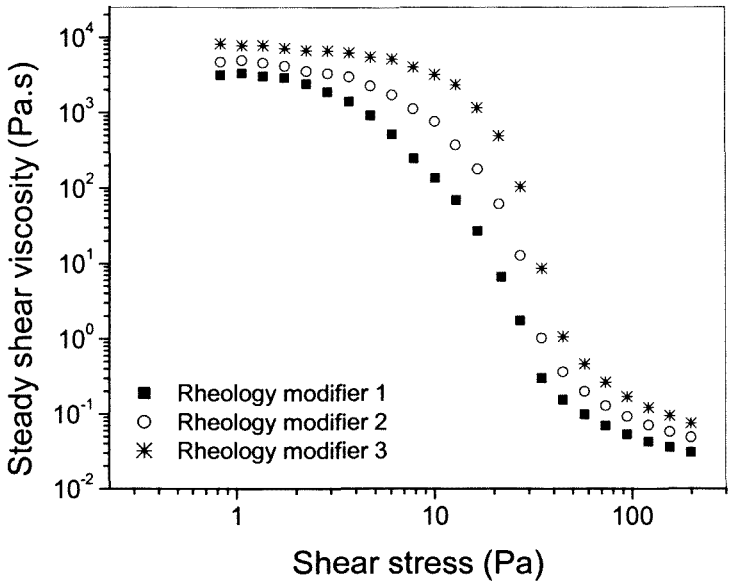


Figure 5.9: Steady shear viscosity for latex solutions thickened with RM 1 – 3.

The initial monomer ratio of MMA:MAA for experiments 7 – 9 was 75:25. The steady shear viscosity profile for the latex solution thickened with RMs 7 – 9 is shown in Figure 5.10. Similar rheology profiles were observed for the latex solutions thickened with RMs 8 and 9, to those of RMs 1 – 3 in Figure 5.9. The rheological behaviour of the conventional alkali-soluble rheology modifiers synthesised in miniemulsion is similar to that of those synthesised in solution as described in Chapters 3 and 4. RMs 4 – 6 were synthesised from the same monomer composition and RAFT agent as RMs 1 – 3, with the only difference being the type of initiator used. The slight differences between the

two groups of rheology modifiers described in Section 5.3.1.1 is not observed in the rheological properties tested, as RMs 4 – 6 give very similar viscosity profiles to those of RMs 1 – 3.

The latex solution thickened with RM 7 shows an almost Newtonian behaviour at very low viscosity. This indicates that the chains were too short, and their MAA content too low, to build any strong intermolecular structure through molecular chain entanglement or hydrodynamic volume thickening. The same low viscosity results can be seen for the rheology profiles of the latex solutions thickened with RMs 10 – 12 (Figure 5.11). For these rheology modifiers, the initial monomer ratios of MMA:MAA were 90:10. RMs 11 and 12 show a small decrease in viscosity at low shear stress indicating that a very small degree of intermolecular structure is present. This is probably due to a small degree of molecular chain entanglement. In the case of RM 10, where the chains are very short, there was no evidence of any significant intermolecular structure. The amount of MAA incorporated in the chains of RMs 10 – 12 was too small for the hydrodynamic thickening mechanism to add any significant contribution to the viscosity of the latex solution.

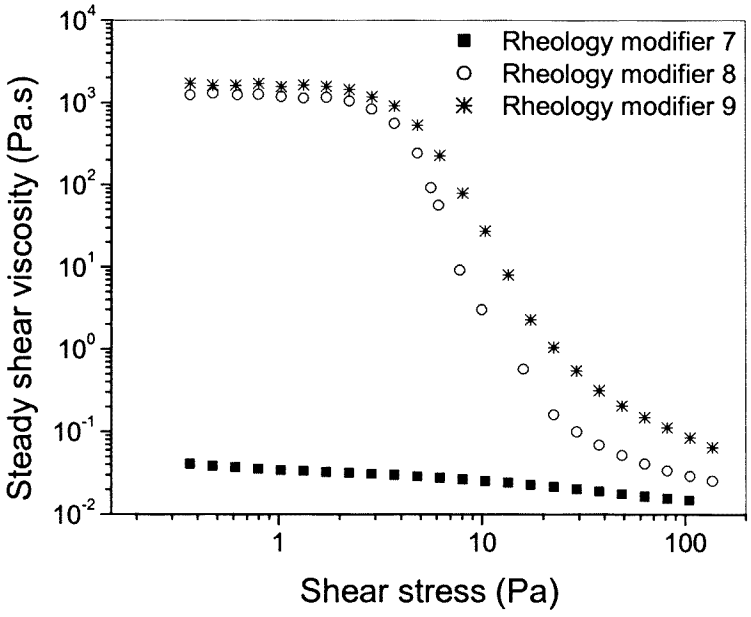


Figure 5.10: Steady shear viscosity for latex solutions thickened with RM 7 – 9.

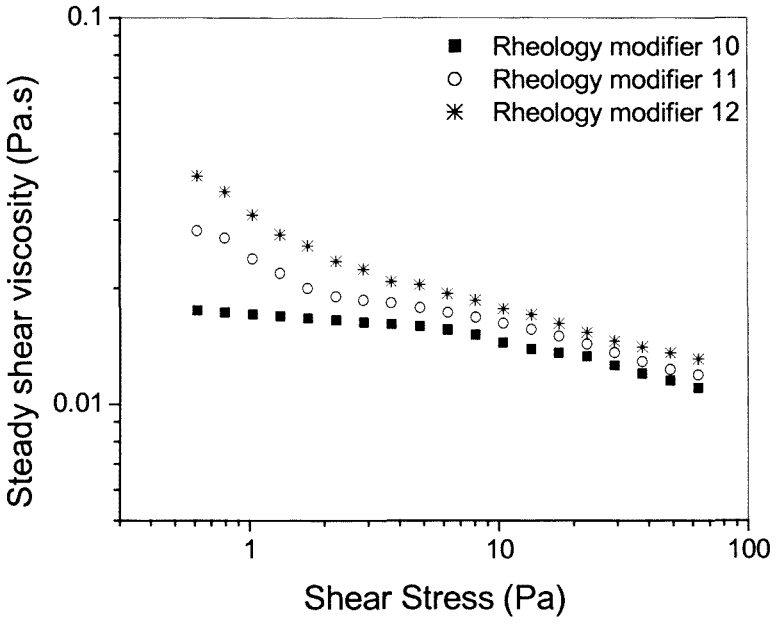


Figure 5.11: Steady shear viscosity for latex solutions thickened with RM 10 – 12.

Figure 5.12 shows the change in the rheology profiles as the amount of MAA incorporated into the polymer chains was decreased. All three of the rheology modifiers have similar molar mass, so any difference between the rheology profiles was probably due to the amount of MAA incorporated. The latex solutions thickened with RM 3 (MMA:MAA, 50:50, $\bar{M}_n$ = 146 000) have both a higher viscosity and higher yield stress than that of the latex solution thickened with rheology modifier 9 (MMA:MAA, 75:25, $\bar{M}_n$ = 129 000). As explained previously, the amount of MAA incorporated into RM 12 (MMA:MAA, 90:10, $\bar{M}_n$ = 127 000) is insufficient to build structure into the latex solution, and therefore the rheology profiles exhibit no detectable yield stress, and have very low viscosity over the entire shear stress range.

The steady shear viscosity data of 15 % polymer solutions of RMs 1 – 3 are presented in Figure 5.13. Similarly to the results observed in Chapter 4, the steady shear viscosity is approximately constant over the entire shear stress range measured (Newtonian behaviour). The viscosity increased as the molar mass increased, because of the increasing degree of chain entanglement. The solution viscosity of the other groups,

containing less MAA, was too low and fell outside the measuring parameters of the rheometer used.

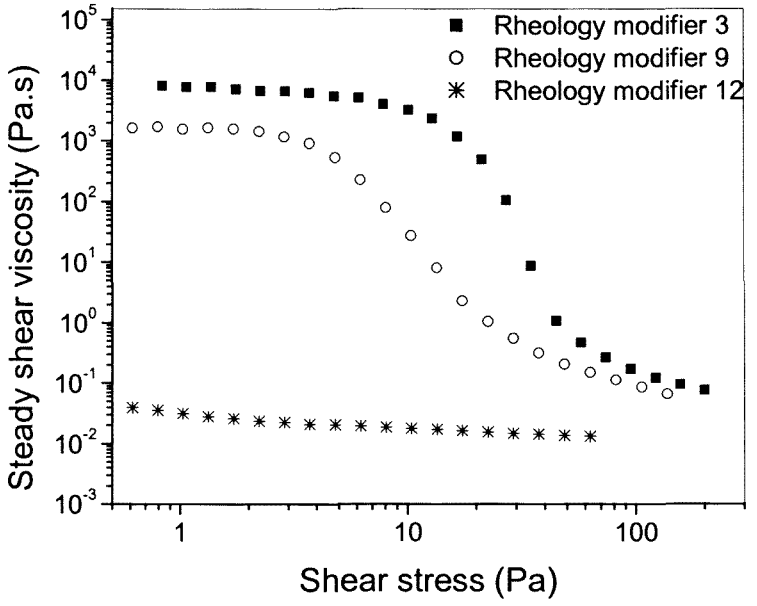


Figure 5.12: Steady shear viscosity for latex solutions thickened with rheology modifiers 3 (MMA:MAA, 50:50), 9 (MMA:MAA, 75:25) and 12 (MMA:MAA, 90:10).

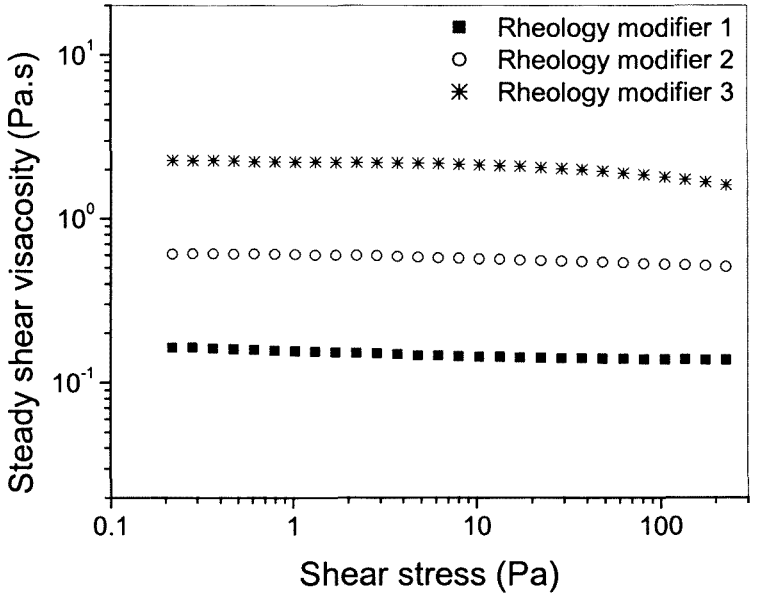


Figure 5.13: The steady shear viscosity data for the 15 % polymer solutions of rheology modifiers 1 – 3. Increasing molar mass from RM 1 to RM 3. See Table 5.3 for molar mass data.

5.3.2.2 Dynamic properties of the conventional rheology modifiers

A dominant storage modulus (G') can be observed over the entire frequency range for the latex solution thickened with RM 1 (Figure 5.14). The dominant storage modulus, that indicates solid-like rheological behaviour for the latex solution, is consistent with the results obtained in Chapters 3 and 4 for conventional rheology modifiers. Also see the conceptual model (Section 3.3.2.1) describing this behaviour.

Figures 5.15 and 5.16 show the effect of an increase in molar mass on the loss and storage moduli of the latex solutions thickened with RMs 1 – 3. It is clear from the dynamic property data in Figures 5.15 and 5.16 that there is an increase in both the loss and storage moduli as the molar mass of the rheology modifiers increases. Once again, the reason for the increase in these moduli is the higher degree of chain entanglement that results from the higher molar mass polymer chains.

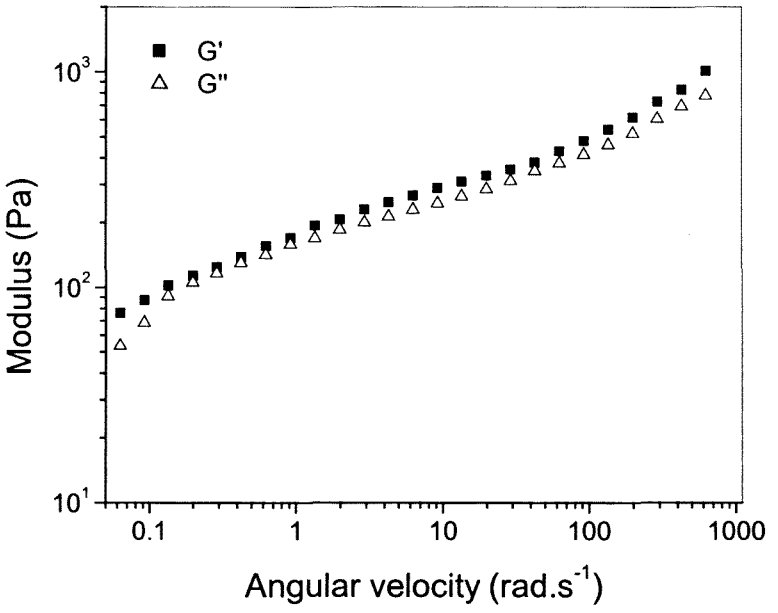


Figure 5.14: Storage and loss moduli of the latex solution thickened with conventional rheology modifier 1.

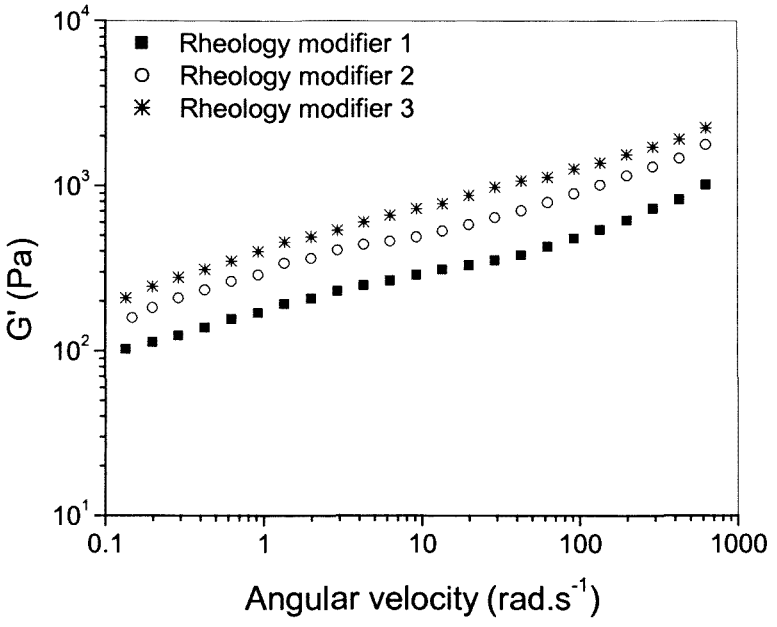


Figure 5.15: Storage modulus of the latex solution thickened with conventional rheology modifiers 1 – 3. Increasing molar mass from RM 1 to RM 3. See Table 5.3 for molar mass data.

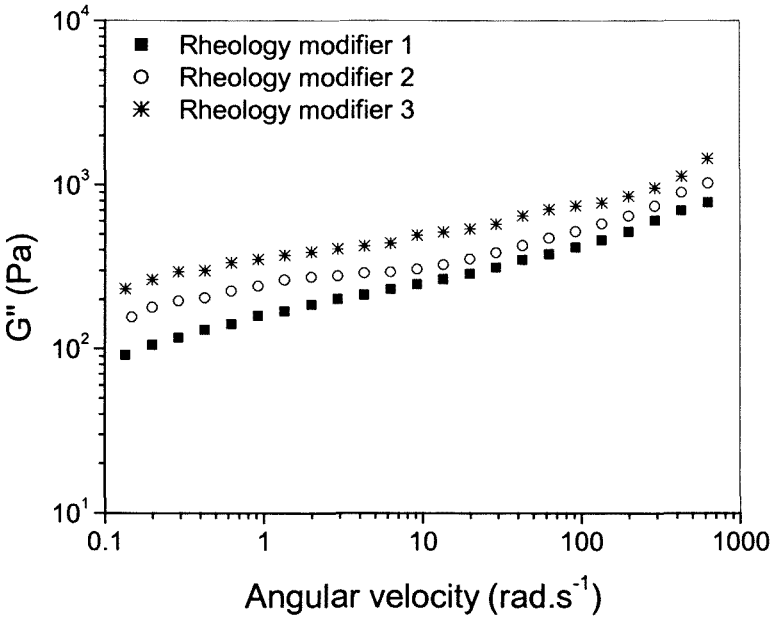


Figure 5.16: Loss modulus of the latex solution thickened with conventional rheology modifiers 1 – 3. Increasing molar mass from RM 1 to RM 3. See Table 5.3 for molar mass data.

5.3.2.3 Associative rheology modifiers

Figure 5.17 shows the steady shear viscosity data for the latex solution thickened with RMs 18 – 20. The molar masses for the three associative rheology modifiers are about the same (Table 5.4). The latex solution thickened with rheology modifier 18, containing only 1% of HM1, shows Newtonian behaviour with very low viscosity values. RMs 19 (2.5 % of HM1) and 20 (5 % of HM1) show similar behaviour, but at much higher viscosities. The viscosity increases significantly as the amount of HM1 is increased from 1 % to 5 %. The reason for this increase in viscosity is due to the hydrophobes interacting with one another and the latex particles, to form intermolecular and intramolecular associations. The higher number of hydrophobic macromonomer units attached to the chain also increases the amount of molecular chain entanglement.

In the latex solutions thickened with RMs 19 and 20, a very strong three-dimensional network is formed, but rheology modifier 18 is not capable of inducing the same strong three-dimensional network, and therefore induces lower viscosity. The formation of this strong three-dimensional network in the latex solution is underlined when one compares the viscosity profiles in Figure 5.17 (associative rheology modifiers) with those of the conventional rheology modifiers in Figure 5.9. The significant decrease in viscosity (yield stress) observed in Figure 5.9 is not present in the rheology profiles of rheology modifier 19 and 20 in Figure 5.17.

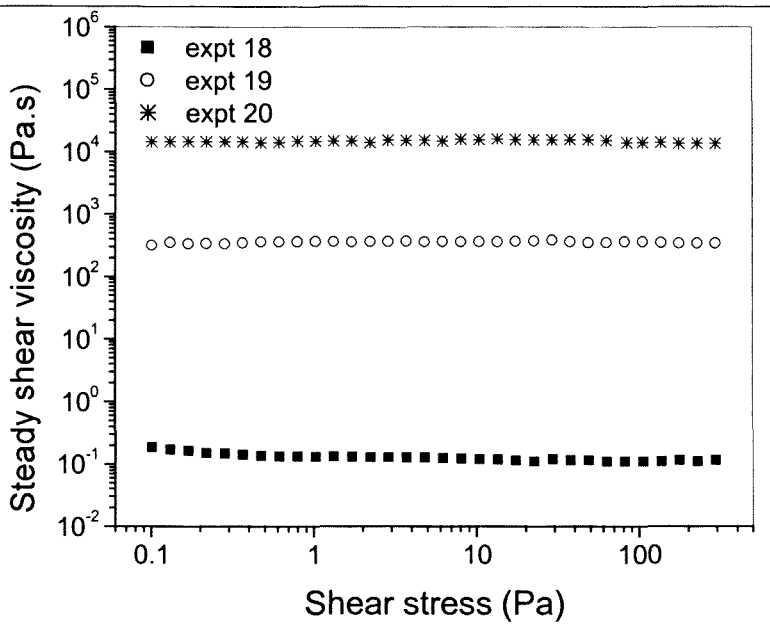


Figure 5.17: Steady shear viscosity for latex solutions thickened with RM18 (1 % HM1), RM19 (2.5 % HM1) and RM20 (5 % HM1).

The steady shear viscosity data for 7.5 % polymer solutions of rheology modifiers 18 – 20 are presented in Figure 5.18. Comparing these rheology profiles to those of the conventional rheology modifiers in Figure 5.13, it is clear that the profiles are similar, but the viscosity is higher for the rheology modifiers in Figure 5.18, which contain various amounts of HM1. It must be noted that the concentration of the conventional rheology modifier solutions in Figure 5.13 is 15 % and the concentration of the associative rheology modifiers in Figure 5.18 is only 7.5 %. It was shown in Section 4.3.3.1 that an increase in concentration leads to higher chain density, which leads to higher chain entanglement, which ultimately leads to an increase in viscosity. So there is a significant increase in the viscosity of the polymer solutions as the amount of HM1 is increased. As explained earlier, this is due to interaction of the hydrophobes with one another and other hydrophobes e.g. latex particles.

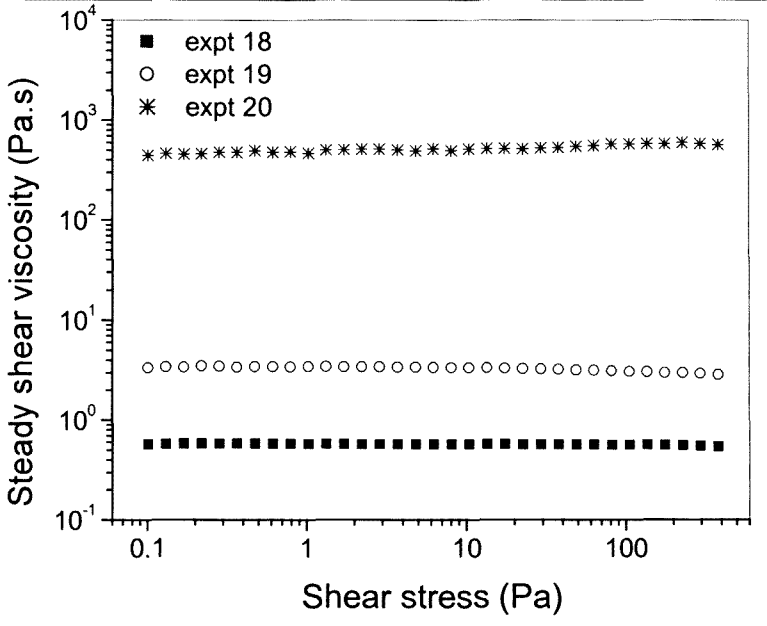


Figure 5.18: The steady shear viscosity data for the 7.5 % polymer solutions of RM18 (1 % HM1), RM19 (2.5 % HM1) and RM20 (5 % HM1).

The dynamic properties (loss and storage moduli) of the latex solutions thickened with associative RMs 18 – 20 are presented in Figures 5.19 – 5.21. A dominant loss modulus (G") over the entire frequency range can be observed in Figure 5.19, for the latex solution thickened with RM 18 that contains 1 % of HM1. Similarly to the steady shear viscosity data for the latex solutions thickened with RM 18 (Figure 5.17), the low modulus values indicate that there is not a significant amount of intermolecular structure built by this rheology modifier. As the amount of HM1 is increased to 2.5 % in rheology modifier 19, there is a large increase in modulus values for the latex solutions thickened by this rheology modifier, but more significantly, there is a cross-over point between G' and G", observable in Figure 5.20. The latex solution in Figure 5.20 shows a dominant storage (G') modulus at high frequency values, with a change to a dominant loss (G") modulus at low frequency values. The latex solution thickened with rheology modifier 20 (5 % HM1) shows a dominant storage modulus (G') over the entire frequency range, in Figure 5.21. Thus, by changing the amount of hydrophobic macromonomer in the polymer chains, it is possible to change the rheological behaviour of the latex solutions from more liquid-like (dominant G") to more solid-like (dominant G').

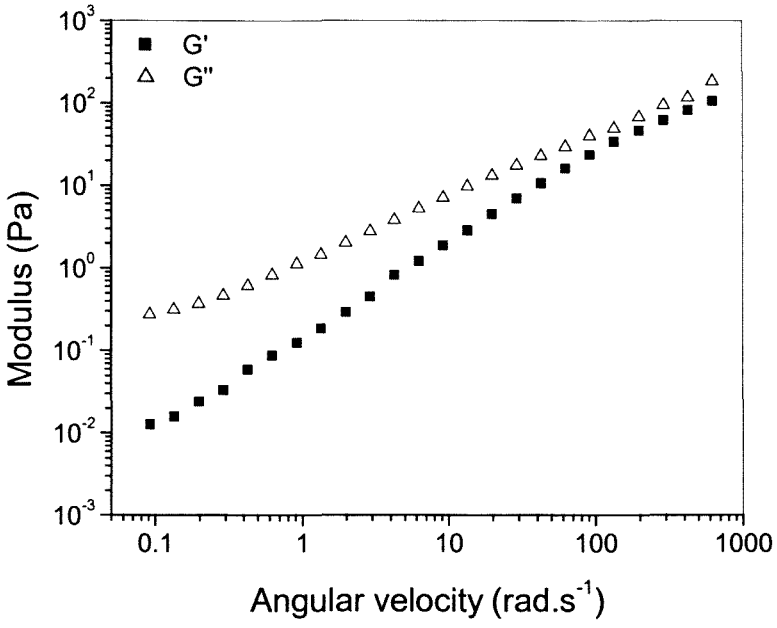


Figure 5.19: Storage and loss moduli of the latex solution thickened with rheology modifier 18 containing 1 % HM1.

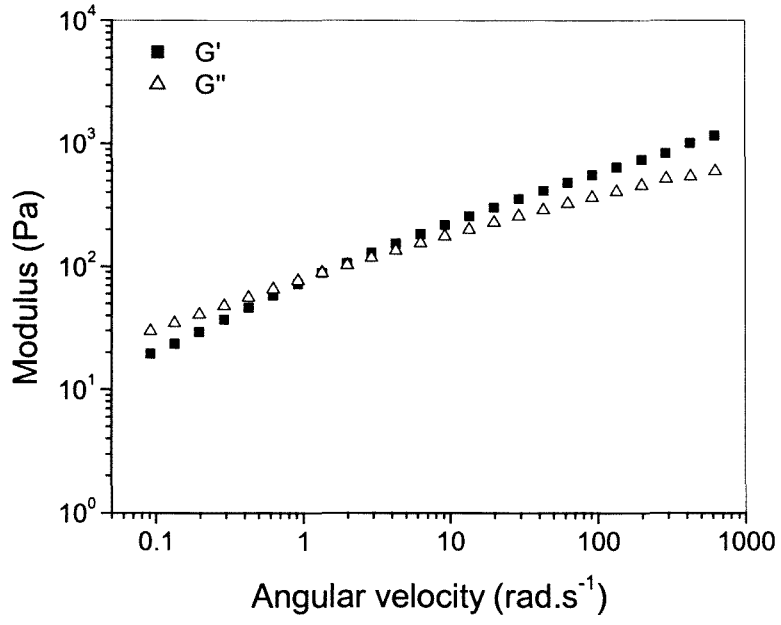


Figure 5.20: Storage and loss moduli of the latex solution thickened with rheology modifier 19 containing 2.5 % HM1.

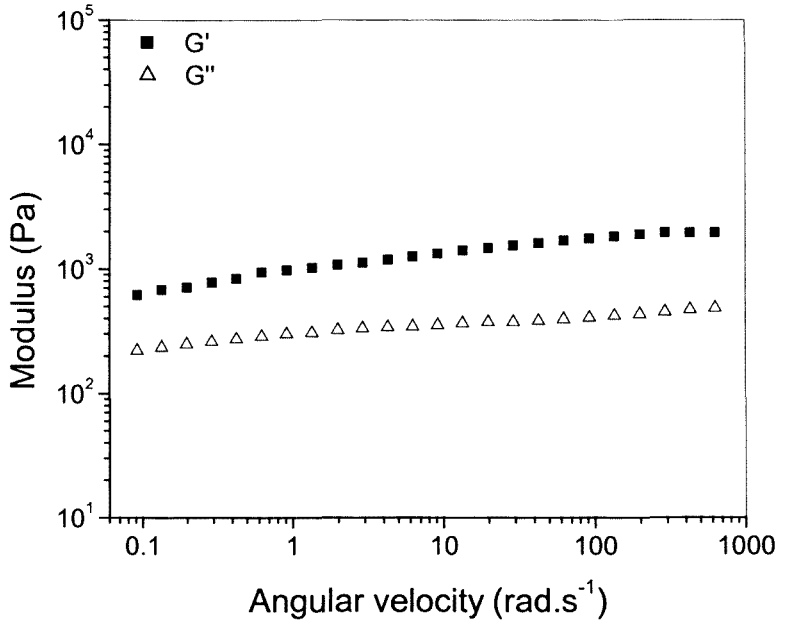


Figure 5.21: Storage and loss moduli of the latex solution thickened with rheology modifier 20 containing 5 % HM1.

5.3 Conclusions

Model alkali-soluble rheology modifiers with well controlled molar mass and narrow molar mass distribution were successfully synthesised using RAFT polymerisation in miniemulsions. The effects that the type of initiator has on the polymerisation reactions were demonstrated by comparative reactions initiated with AIBN (oil-soluble) or KPS (water-soluble). The polymerisation rate for reactions initiated with KPS was almost double that of the AIBN initiated reactions. This is probably due to the higher concentration of KPS in the water phase, resulting in a greater rate of entry and therefore a higher overall propagating radical concentration. Since AIBN is oil-soluble, only a small fraction is dissolved in the water phase. On the basis of the conclusions of Luo *et al.*,[38] that in the case of polymer particles with diameters up to approximately 100 nm (as is the case here), it was expected that most of the polymerisation for this system would be initiated from free radicals originating in the water phase. The experimental molar mass values for the AIBN initiated reaction follow the predicted theoretical values more closely than did the KPS initiated reactions. The reason for the deviation from the

theoretical values and the broader polydispersities was probably due to the higher initiator efficiency in the KPS initiated reactions.

As the percentage of monomer MAA in the initial feed was decreased, there was a decrease in the polymerisation rate. This is because the propagation rate constant (k_p) for MAA is higher than that of MMA, leading to a lower rate of polymerisation when the percentage of MAA was decreased.

The steady shear viscosity data for latex solutions thickened with the conventional rheology modifiers containing a 50:50 ratio of MMA:MAA showed the typical drop in viscosity (as seen in Chapter 3) at a critical shear stress (yield stress). An increase in molar mass leads to an increase in the viscosity and the yield stress due to a higher degree of chain entanglement. Due to the fact that conventional thickeners rely on the hydrodynamic thickening mechanism to build structure, this significant drop in viscosity with a decreasing MAA incorporation into the chains was not unusual.

Associative alkali-soluble rheology modifiers were synthesised by incorporating HM1 into the polymer chains. This was not successfully done for HM2 – HM4. Associative rheology modifiers 19 and 20 containing 2.5 % and 5% of HM1 respectively showed steady shear viscosity data representing very strong three-dimensional network formation. The latex solutions thickened with the associative rheology modifiers showed high viscosity over the entire measured shear stress range, which is in contrast to the behaviour observed for the conventional rheology modifiers. The viscosity increased as the percentage of HM1 incorporated increased from 1% to 5%. The dynamic properties of the latex solutions thickened with the three associative rheology modifiers changed from liquid-like in behaviour (dominant G") for rheology modifier 18 to solid-like behaviour (dominant G') for rheology modifier 20. The larger amount of hydrophobic macromonomers increases intermolecular and intramolecular association between the hydrophobes, which builds structure; additionally, there is an increased degree of chain entanglement.

The rheological properties of the conventional rheology modifiers synthesised in Chapters 3 (solution), 4 (solution) and 5 (miniemulsion) show very similar results. The miniemulsion system however has the advantages of higher final conversion, no solvent

removal is required, and faster reaction times. A major drawback for the miniemulsion system is the fact that it was not possible to synthesise associative rheology modifiers containing HM2, HM3, or HM4.

5.4 References

1 Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*, Academic Press, London, 1995, 51.

2 Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*, Wiley and Sons, New York, 1999, 37.

3 Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* 1997, 30, 2071.

4 Marestin, C.; Noel, C.; Guyot, A.; Claverie, J. *Macromolecules* 1998, 31, 4041.

5 Prodpran, T.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *Macromol. Symp.* 2000, 155, 1.

6 Macleod, P. J.; Barber, R.; Odell, P. G.; Keoshkerian, B.; Georges, M. K. *Macromol. Symp.* 2000, 155, 31.

7 Farcet, C.; Lansalot, M.; Charleux, B.; Pirri, R.; Vairon, J. P. *Macromolecules* 2000, 33, 8559.

8 Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* 1998, 31, 5951.

9 Qiu, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 1999, 32, 2872.

10 Qiu, J.; Pintauer, T.; Gaynor, S. G.; Matyjaszewski, K.; Charleux, B.; Pirri, R.; Vairon, J. P. *Macromolecules* 2000, 33, 7310.

11 Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Part A: Polym. Chem.* 2000, 38, 4724.

12 Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J. P.; Pirri, R. *Macromolecules* 1999, 32, 2537.

13 Butté, A.; Storti, G.; Morbidelli, M. *Macromolecules* 2000, 33, 3485.

14 Farcet, C.; Lansalot, M.; Pirri, R.; Vairon, J. P.; Charleux, B. *Macromol. Rapid. Commun.* 2000, 21, 921.

15 Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* 2000, 150, 33-38.

16 Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* 2000, 150, 23.

17 Moad, G.; Chiefari, J.; Chong, B. Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* 2000, 49, 993.

18 Monteiro, M. J.; Sjoberg, M.; van der Vlist, J.; Gottgens, C. M. *J. Polym. Sci., Part A: Polym. Chem.* 2000, 38, 4206.

19 De Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* 2000, 33, 9239.

20 Vosloo, J. J.; de Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* 2002, 35, 4894.

21 Maxwell, I. A.; Morrison, B. R.; Gilbert, R. B. *Macromolecules* 1991, 24, 1629.

22 Mishchuk, N. A. *J. Dispersion Sci. Techn.* 1997, 18, 517.

23 Webster, A. J.; Cates, M. E. *Langmuir* 1998, 14, 2068.

24 Landfester, K.; Bechthold, N.; Forster, S.; Antonetti, M. *Macromol. Rapid. Commun.* 1999, 20, 81.

25 Walstra, P. *Chem. Eng. Sci.* 1993, 48, 333.

26 Friberg, S. E.; Jones, S. *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1994, 9, 393.

27 Landfester, K. *Macromol. Rapid. Commun.* 2001, 22, 896.

28 Choi, Y. T.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci. Polym. Chem.* Ed. 1985, 23, 2973.

29 Reimers, J.; Schork, F. J. *J. Appl. Polym. Chem.* 1995, 33, 1391.

30 Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol* 1976, 49, 536.

31 Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* 2002, 35, 7582.

32 Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.

33 Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.

34 Chern, C.-S.; Sheu, J.-C. *Polymer* 2001, 42, 2349.

35 Butté, A.; Storti, G.; Morbidelli, M. *Macromolecules* 2001, 34, 5885.

36 Monteiro, M. J.; Hodgson, M.; De Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* 2000, 38, 3864.

37 Alducin, J. A.; Forcada, J.; Barandiaran, M. J.; Asua, J. M. *J. Polym. Sci., Part A: Polym. Chem.* 1991, 29, 1265.

38 Luo, Y.; Schork, F. J. *J. Polym. Sci., Part A: Polym. Chem.* 2002, 40, 3200.

39 Edelhauser, H.; Breitenbach, J. W. *J. Polym. Sci., Part A: Polym. Chem.* 1959, 35, 423.

40 Breitenbach, J. W.; Edelhauser, H. *Makromol Chem* 1967, 44, 196.

41 Barton, J.; Karpatyova, A. *Makromol Chem* 1987, 188, 693.

42 Nomura, M.; Fujita, K. *Makromol Chem Rapid Commun* 1989, 10, 581.

43 Nomura, M.; Ikoma, J.; Fujita, K. *ACS Symposium Series* 492, 1993, 55.

44 Asua, J. M.; Rodrgues, V. S.; Sudol, E. D.; El-Aasser, M. S. J. *Polym. Sci., Part A: Polym. Chem.* 1989, 27, 3569.

45 Blythe, P. J.; Klein, A.; Phililips, J. A.; Sudol, E. D.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* 1999, 37, 4449.

46 Yamaoka, H.; Nagta, K.; Ikeda, T.; Okamura, S. *Radiat. Phys. Chem.* 1981, 18, 1073.

47 Torikai, A.; Kato, H.; Kuri, Z.-I. *J. Polym. Sci., Part A: Polym. Chem.* 1976, 14, 1065.

48 Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* 1993, 26, 6410.

49 LeSota, S.; Lewndowski, E. W.; Schaller, E. J. *J. Coat. Technol.* 1989, 61, 135.

CHAPTER 6

Conclusions

The main conclusions of this research endeavour into assessing the structure/property relationship of model alkali-soluble rheology modifiers synthesised via the RAFT process are as follows.

Chapter 3 The synthesis of conventional and associative rheology modifiers via the *in situ* RAFT solution polymerisation using AIBN, bis(thiocarbonyl) disulfide, methyl methacrylate, methacrylic acid and hydrophobic macromonomers was successfully carried out. It was found that these polymers had well-controlled molar mass, controlled molar mass distribution and the polymer had the ability to chain extend to form AB block copolymers. Conventional and four associative rheology modifiers of three different molar masses were synthesised. Three of the associative rheology modifiers (varying molar mass) contained HM4 (100 ethylene oxide spacer units) and the fourth one contained HM1 (5 ethylene oxide spacer units). An AB block copolymer was also synthesised in which case HM4 was added to one end of the polymer chains (block A, conventional rheology modifier) as the B block. All of the polymers had molar mass polydispersities < 1.6. Some limitations for these solution polymerisation reactions were observed such as a conversion limit of about 60 % and the fact that the experimental number average molar mass results obtained were higher than the predicted molar masses. The higher experimental molar masses obtained were probably due to the mechanism of the *in situ* RAFT formation process, which results in a lower amount of RAFT agent available than was initially added.

The rheology modifiers were tested in a well-characterised core shell emulsion and each of the rheology modifiers synthesised gave the latex solution their own specific rheology profile. The steady shear viscosity data for the latex solutions thickened with the conventional rheology modifiers showed a very significant drop in viscosity at a critical shear stress (yield stress) in the rheology profile. An increase in the molar mass led to an

increase in the overall viscosity as well as an increase in the yield stress. This specific rheology profile of the conventional rheology modifiers is due to their hydrodynamic thickening mechanism. In the case of the latex solutions thickened with associative rheology modifiers, there was also a decrease in viscosity as the shear stress was increased, but no large drop in viscosity was present (no yield stress). The associative rheology modifiers follow a dual thickening mechanism (hydrodynamically and associatively), which explains the different rheology profiles observed compared with those of the conventional rheology modifiers. In both conventional and associative rheology modifiers, an increase in molar mass leads to a higher degree of chain entanglement, which then leads to an increase in the viscosity.

The latex solutions thickened with the conventional and associative rheology modifiers showed contrasting dynamic properties. The conventional rheology modifiers gave the latex solutions a more solid-like behaviour (dominant G') compared to the associative rheology modifiers that gave a more liquid-like behaviour (dominant G").

In the case of the synthesis of the AB block copolymers it was shown that by addition of the hydrophobic macromonomer to only one end of the polymer chain, it is possible to obtain qualitatively intermediate rheology results between those obtained with conventional rheology modifiers and those with the associative rheology modifiers.

Chapter 4 The alkali-soluble rheology modifiers where synthesised in solution using 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid as RAFT agent. Different associative rheology modifiers where synthesised containing hydrophobic macromonomers with varying numbers of ethylene oxide spacer units. The three hydrophobic macromonomers used contained 20 (HM2), 50 (HM3) and 100 (HM4) ethylene oxide units. For each of the different hydrophobic macromonomers three polymers of different molar masses were synthesised. All polymers synthesised showed well-controlled molar mass (18 000 – 51000 $g.mol^{-1}$) and narrow molar mass polydispersities (< 1.5). Changing the number of ethylene oxide spacer units in the hydrophobic macromonomers did not significantly affect the amount of macromonomers that were incorporated per polymer chain.

The Herschel-Bulkley model and the Carreau model well described the different types of rheology profiles given to the latex solutions by the conventional and associative rheology modifiers, respectively. The performances of the associative rheology modifiers were influenced to a much greater extent by the number of ethylene oxide spacer units between the terminal hydrophobe and the polymer backbone than they were by the variation of the molar masses of the polymers.

As the number of ethylene oxide spacer units was increased from 20 to 100 there was a significant increase in the zero shear viscosity of the latex solutions thickened with the different associative rheology modifiers. Contrasting results were obtained for the polymer solution (no core-shell latex present), where the associative rheology modifiers containing the highest number (EO = 100) of ethylene oxide spacer units gave the lowest viscosity, but the rheology modifiers containing the 50 ethylene oxide spacer units gave the highest steady shear viscosity.

The contrasting rheological behaviour of the associative rheology modifiers in the latex-solution and alkali-solution was due to the preferable and/or stronger association of the terminal hydrophobes with the latex particles than with other terminal hydrophobic groups. In alkali solution, the only possible association that the terminal hydrophobic groups can form is with other hydrophobic groups on the same chain or on other polymer chains, since no latex particles are present.

Chapter 5 Conventional and associative rheology modifiers with well-controlled molar mass and narrow molar mass polydispersities were successfully synthesised using RAFT (4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid) in free radical miniemulsion reactions. All of the miniemulsions showed good colloidal stability over a period of a minimum of several months.

The polymerisation rate of the KPS (water-soluble) initiated reactions was almost double that of the AIBN (oil-soluble) initiated reactions. It was expected that the initiation rate for the AIBN system would be lower, leading to lower polymerisation rates, as observed. The KPS initiated reactions showed experimental molar mass values that were lower than the theoretical values calculated, and showed slightly broader polydispersities. The

reason for the deviation from the theoretical values and the broader polydispersities was probably due to the higher initiator efficiency in the KPS initiated reactions.

There was a decrease in the polymerisation rate as the percentage of MAA in the overall amount of monomer used was decreased. The reason for the decrease in the polymerisation rate is because the propagation rate constant (k_p) for MAA is higher than that of MMA and therefore a decrease in the percentage of MAA results in a decrease in the polymerisation rate.

The steady shear viscosity data for latex solutions thickened with the conventional rheology modifiers containing a 50:50 ratio of MMA:MAA showed the typical sudden drop in viscosity at a critical shear stress (yield stress). An increase in the molar mass results in a higher degree of chain entanglement that leads to an increase in the viscosity and the yield stress. The large decrease in the viscosity, as the amount of MAA was decreased, was because the conventional rheology modifiers relied on the hydrodynamic thickening mechanism to build structure.

The latex solutions thickened with associative rheology modifiers showed no sudden drop (corresponding to a yield stress) in the viscosity over the measured shear stress range, and there was a significant increase in the steady shear viscosity as the amount of incorporated HM1 was increased from 1% to 5%. The dynamic properties of the latex solutions thickened with the three different associative rheology modifiers changed from liquid-like in behaviour (dominant G") to solid-like behaviour (dominant G') as the amount of HM1 incorporated was increased from 1% to 5%.

The increasing amount of hydrophobic macromonomer, from 1 – 5% incorporation, increased intermolecular and intramolecular association between the hydrophobes. This association builds an increasingly strong three-dimensional structure with increasing hydrophobic macromonomer content, which, with an increased degree of chain entanglement, leads to higher viscosity and more solid-like behaviour.

The rheological properties of the conventional rheology modifiers synthesised in Chapters 3 (solution), 4 (solution) and 5 (miniemulsion) show very similar results. The miniemulsion system however has the advantage of higher final conversion, no solvent removal is required and faster reaction times. A major drawback for the miniemulsion

system is the fact that it was not possible to synthesise associative rheology modifiers, containing HM2, HM3 and HM4.

This study has shown that it is possible to synthesise alkali-soluble rheology modifiers of predetermined molar mass, narrow molar mass distribution and tailored architecture by means of the RAFT process. Being able to control the architecture of the rheology modifier and knowing its structure/property relationship gives one the tool to design a rheology modifier that will give the necessary rheological properties desired, for the specific end application.

Future work:

It has been shown in this research endeavour that it is possible to synthesise different alkali-soluble rheology modifiers of controlled architecture and molar mass, which have their own unique rheology properties. This was only the first step in understanding the structure/property relationship of alkali-soluble rheology modifiers and with the synthesis of more complex architectures one will be able to obtain a more diverse range of rheology modifiers.

- The synthesis of alkali-soluble rheology modifiers with star-shaped structures.
- Investigating the structure/property relationship of these star-shaped rheology modifiers. The star-shaped structures could most probably introduce new types of rheology profiles.
- Optimising the miniemulsion system, to see if it is not possible to synthesise associative rheology modifiers containing HM2, HM3 and HM4.
- To investigate the synthesis of higher molar mass (>300 000) polymers via the RAFT process. This will enable one to make direct comparisons to commercially available alkali-soluble rheology modifiers which have higher molar masses. This could possibly be a very tricky problem, since there are no reports in literature of such high molar mass polymers synthesised by the RAFT process.

Appendix A

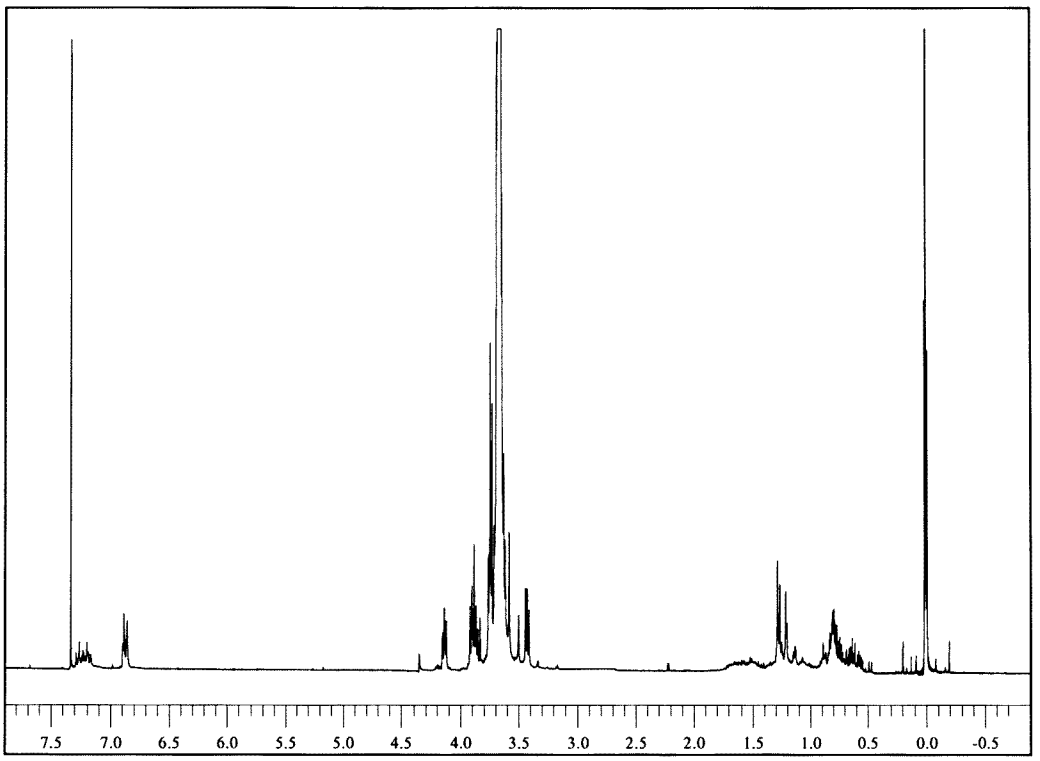


Figure A.1: ^{1}H NMR spectrum of nonionic surfactant.

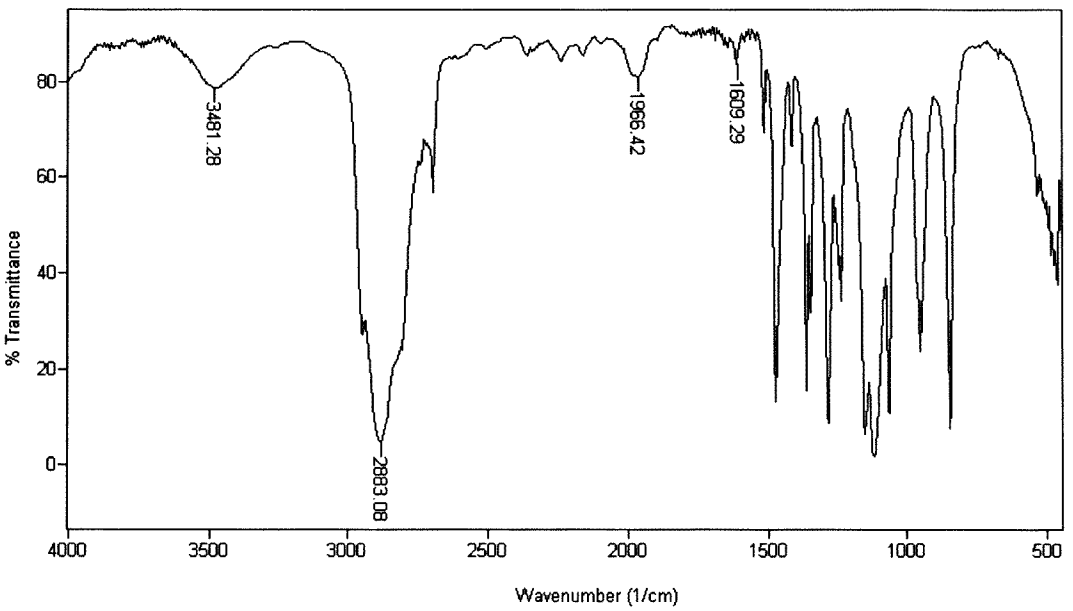


Figure A.2: FTIR spectrum of the nonionic surfactant.

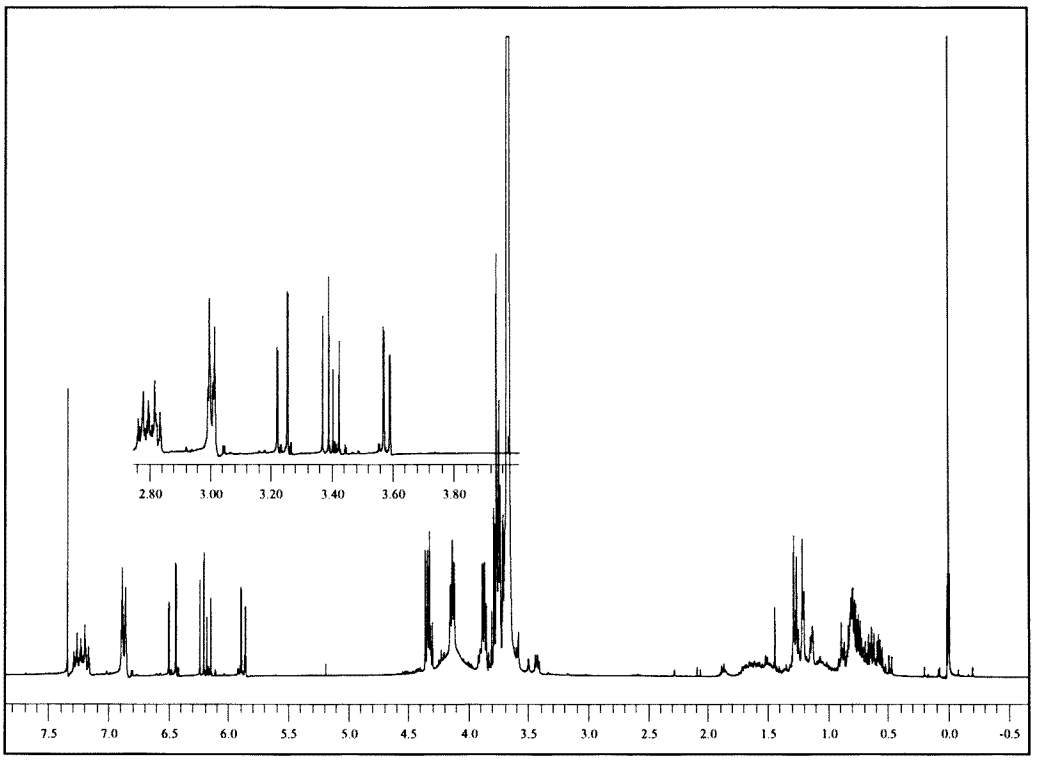


Figure A.3: ^{1}H NMR spectrum of the hydrophobic macromonomer.

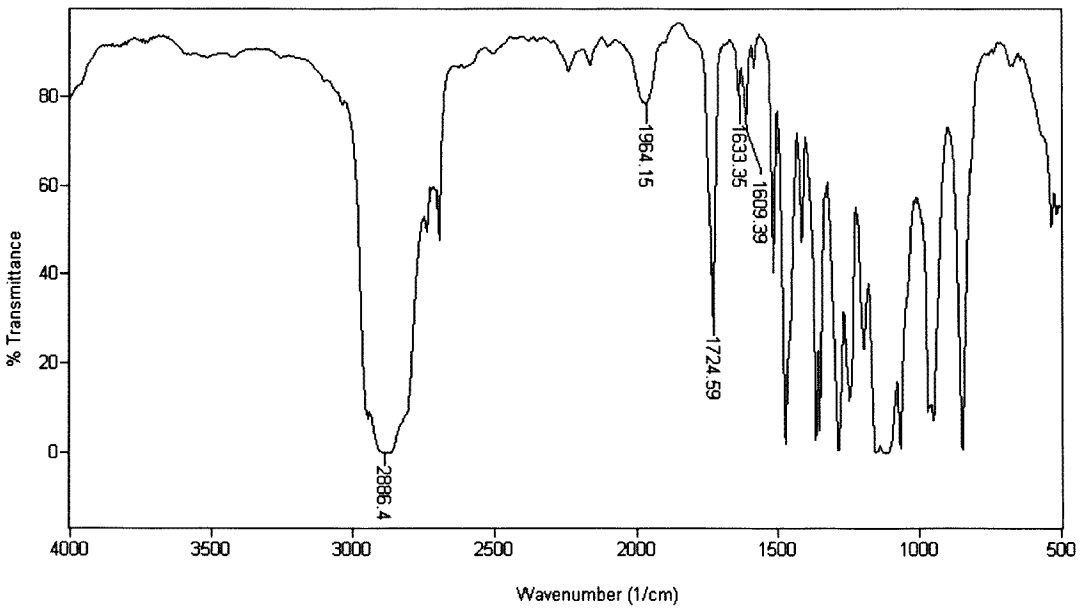


Figure A.4: FTIR spectrum of the hydrophobic macromonomer.

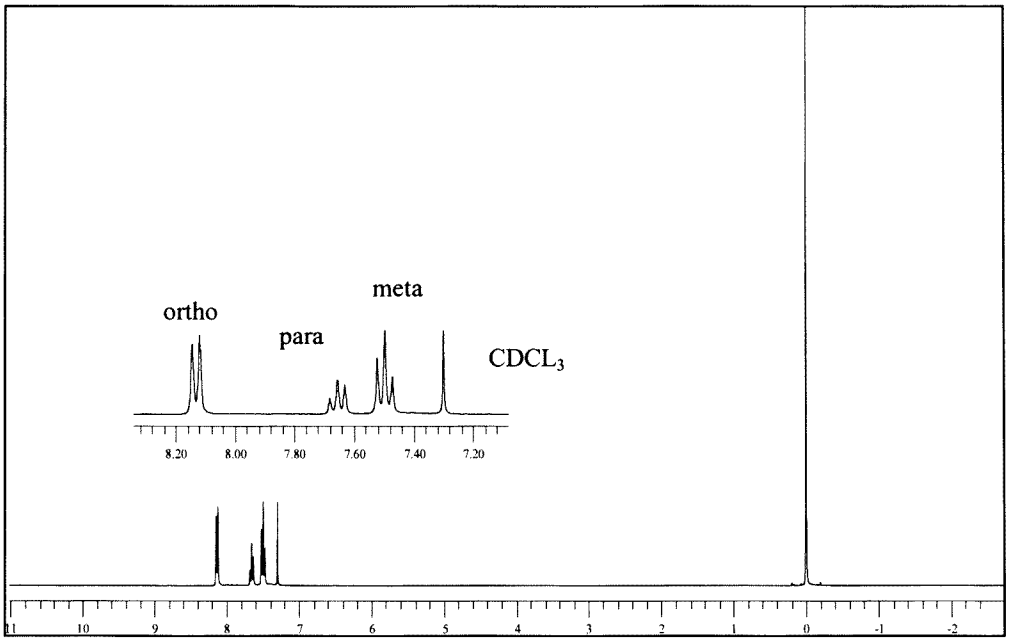


Figure A.5: ^{1}H NMR spectra of bis(thiocarbonyl) disulfide.

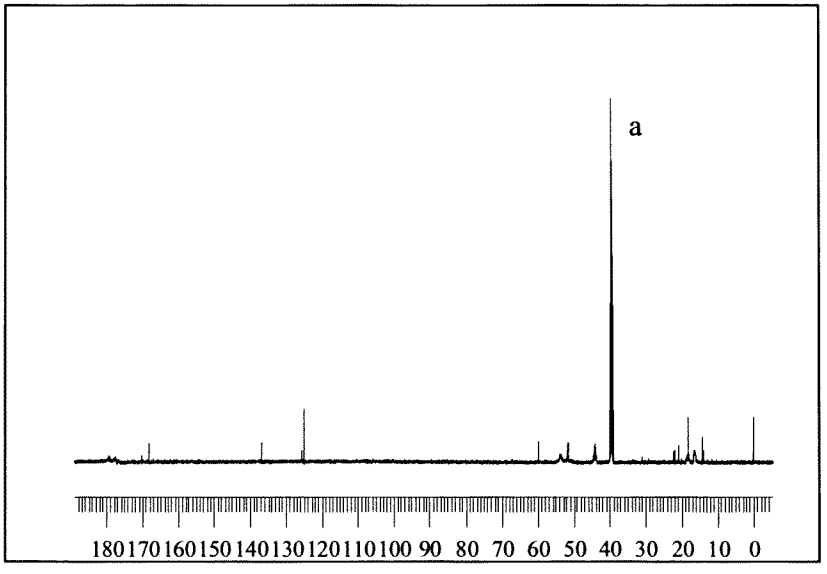


Figure A.6: ^{13}C-NMR spectra of conventional rheology modifier 7.

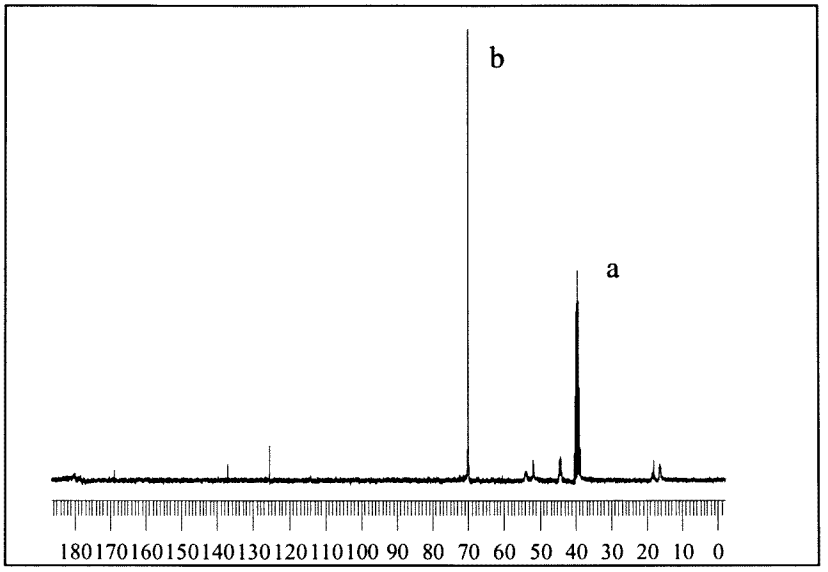


Figure A.7: ^{13}C-NMR spectra of associative rheology modifier 8.

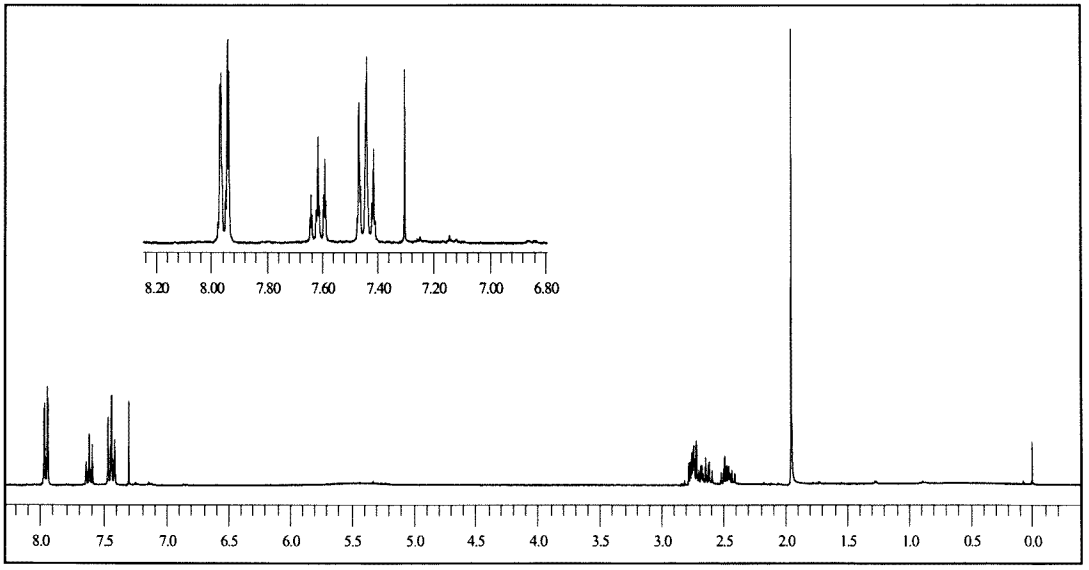


Figure A.8: ^{1}H NMR spectra of 4-cyanao-4-((thiobenzoyl)sulfanyl)pentanoic acid.